A COMPLETE COURSE IN

I.S.C.

# Chemistry

VOL. II

V. P. SAXENA

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# A
# COMPLETE COURSE
# IN
# I.S.C. CHEMISTRY
## VOL. II

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COVERING THE SYLLABUS IN CHEMISTRY PRESCRIBED BY THE COUNCIL FOR INDIAN SCHOOL CERTIFICATE EXAMINATIONS, NEW DELHI FOR I.S.C. (XI-XII) EXAMINATIONS, 1986 AND ONWARDS.

# A COMPLETE COURSE
# IN
# I.S.C. CHEMISTRY

## VOLUME II
## FOR CLASS XII

By

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Library

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# Preface to the New Edition

I.S.C. Chemistry, Volume II has been reshaped to meet the requirements of the latest syllabus in Chemistry (*Principal Level*) prescribed by the Council for Indian School Certificate Examination for standard XII. The book is divided in three parts covering topics in Physical Chemistry, Inorganic Chemistry, and Organic Chemistry respectively. Many chapters have been suitably modified while a few others have been almost completely rewritten. The general style of the presentation of the subject matter continues to be essentially the same as in the author's other well known text books corresponding to the syllabi prescribed by the Council for junior level, *viz.*, '*Exploring Chemistry*' for classes VII and VIII and '*A New Certificate Chemistry*' for classes IX and X. Much care has been taken to explain the abstract ideas and theories of Chemistry, which often tend to elude comprehension, in a systematic manner and by bringing out their releavnce to the experiences and applications in everyday life so that there should be little difficulty in acquiring a clear understanding. The treatment of the subject matter is exhaustive, yet, to the point, and the text is extensively illustrated with line drawings for their great learning value. A large number of *solved numerical problems* have been given in relevant chapters to provide thorough grounding in solving similar problems.

In keeping with the latest trends in the teaching of Chemistry more emphasis has been laid on the "*whys and hows*" rather than on the mere '*whats*' of the various chemical phenomena throughout the course of the text. Serious effort has been made to highlight how the physical properties and chemical behaviour of the elements and their chemical compounds can be related to the electric configurations, and how this relationship gives a certain coherence to the Chemistry of the elements.

A large number of problems and questions pertaining to the topic are given at the end of each chapter. These have been constructed and selected to ensure that they would test not only the factual knowledge pertaining to the topic but also the higher abilities of critical thinking, reasoning, and imagination, and would enable the students to detect the specific areas in which they have failed to reach the proper level of apprehension. Useful hints have been provided for solving certain selected questions which an average student may find rather difficult to attempt.

I earnestly hope that the present book will significantly help the students in studying Chemistry with intelligent interest, thrill of exploration, and a clear understanding of the various concepts. Despite best efforts, however, there might be errors of commission or omission and I shall feel highly obliged if these are brought to my notice. Any suggestions for the improvement of the book and guiding its development through subsequent editions will be gratefully received and acknowledged.

VED PRAKASH SAXENA

## REVISED SYLLABUS IN CHEMISTRY PRESCRIBED BY THE COUNCIL FOR I.S.C. EXAMINATIONS, NEW DELHI, FOR I.S.C. STANDARD XII

**One Theory Paper** *(3 hours)*

**One Practical Paper** *(3 hours)*

### THEORY

### SECTION A

**Atomic Structure**

1.1. Electrons, protons and neutrons as the fundamental particles of major importance in chemistry ; their charges and relative masses.

2.2. (*a*) The nucleus of the atom ; isotopes and mass number. The detection of $\alpha$- and $\beta$-particles and $\gamma$-rays : the nature of $\alpha$- and $\beta$-particles ; evidence from the experiments with photographic emulsions and cloud chambers and from the differenecs in penetrating ability to establish the nature of the rays should be mentioned and treated qualitatively, but detailed treatment is not intended ; Rutherford's experiment. See also Section 7 of this syllabus.

(*b*) The relation between the convergence limit of the Lyman-series and the ionisation energy of the hydrogen atom should be appreciated. The concept of electronic energy levels should be developed from data available on ionisation energies of lighter atoms.

Quantum numbers and the Pauli exclusion principle to be included. For a systematic approach the following are included :

(*i*) Rutherford's experiment,

(*ii*) Bohr's atomic model,

(*iii*) Simple concept of orbitals,

(*iv*) Atomic spectra (differences of continuous and discontinuous spectra),

(*v*) Study of Hydrogen spectra (to show that electrons are situated at certain fixed distance energy levels and not distributed randomly about the nucleus),

(*vi*) Lyman-series, Balmer-series, Paschen-series, Brackett-series, and Pfund-series.

Convergence limit of Lyman-series and other series, and ionisation energy must be mentioned. Questions will not be set on the *last four* series.

(*vii*) The Pauli exclusion principle regarding the structure of the atom Quantum number should be treated in detail. (Quantum numbers are very much related to energy levels, sub-energy levels and orbitals).

(*viii*) The size, shape and orientation of orbitals must be mentioned to represent the electronic configuration of the atom (representation in terms of s, p, and d orbitals) e.g. $Cl=2.8.7=1s^2, 2s^2, 2px^2\ 2py^3\ 2pz^2, 3s^2\ 3p^5$.

2. The Periodic Table

(*a*) Atomic number as the basis for classification of the elements in the Periodic Table. Questions will not be set on the historical development of the Periodic Table.

(*b*) Extra nuclear structure as the basis of perodicity. Some idea of the following :

Ionisation potential, Electron affinity, Atomic radius, Atomic Volume etc., must be given.

The periodicity of electronic structure leading to the periodicity of chemical elements e.g., the relative ease of ionisation of the elements.

| 1 | 2 | | | | | | | | | | | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1<br>H | | | | | | | | | | | | | | | | 1<br>H | 2<br>He |
| 3<br>Li | 4<br>Be | | | | | | | | | | | 5<br>B | 6<br>C | 7<br>N | 8<br>O | 9<br>F | 10<br>Ne |
| 11<br>Na | 12<br>Mg | | | | | | | | | | | 13<br>Al | 14<br>Si | 15<br>P | 16<br>S | 17<br>Cl | 18<br>Ar |
| 19<br>K | 20<br>Ca | 21<br>Sc | 22<br>Ti | 23<br>V | 24<br>Cr | 25<br>Mn | 26<br>Fe | 27<br>Co | 28<br>Ni | 29<br>Cu | 30<br>Zn | 31<br>Ga | 32<br>Ge | 33<br>As | 34<br>Se | 35<br>Br | 36<br>Kr |
| 37<br>Rb | 38<br>Sr | 39<br>Y | 40<br>Zr | 41<br>Nb | 42<br>Mo | 43<br>Tc | 44<br>Ru | 45<br>Rh | 46<br>Pd | 47<br>Ag | 48<br>Cd | 49<br>In | 50<br>Sn | 51<br>Sb | 52<br>Te | 53<br>I | 54<br>Xe |
| 55<br>Cs | 56<br>Ba | 57<br>—<br>71 | 72<br>Hf | 73<br>Ta | 74<br>W | 75<br>Re | 76<br>Os | 77<br>Ir | 78<br>Pt | 79<br>Au | 80<br>Hg | 81<br>Tl | 82<br>Pb | 83<br>Bi | 84<br>Po | 85<br>At | 86<br>Rn |
| 87<br>Fr | 88<br>Ra | 89<br>—<br>103 | | | | | | | | | | | | | | | |
| | | | 57<br>La | 58<br>Ce | 59<br>Pr | 60<br>Nd | 61<br>Pm | 62<br>Sm | 63<br>Eu | 64<br>Gd | 65<br>Tb | 66<br>Dy | 67<br>Ho | 68<br>Er | 69<br>Tm | 70<br>Yb | 71<br>Lu |
| | | | 89<br>Ac | 90<br>Th | 91<br>Pa | 92<br>U | 93<br>Np | 94<br>Pu | 95<br>Am | 96<br>Cm | 97<br>Bk | 98<br>Cf | 99<br>Es | 100<br>Fm | 101<br>Md | 102<br>No | 103<br>Lr |

(*c*) Periodicity of elements with reference to s, p, d and f block elements.

3. Phase equilibria.

Enantiotropy and Monotropy are included.

Study of variation of vapour pressure of a pure liquid with temperature.

Boiling point. Steam distillation boiling point diagrams for liquid mixtures (including azeotropes). Fractional distillation. Freezing point diagrams for liquid mixtures forming simple eutectics.

Study of phase rule with its applications to (*i*) one component, (*ii*) two component systems is expected.

3.1. Solubility of gases in liquids.

Henry's law (derivation not required) ; a qualitative explanation of Henry's law in terms of Le Chatelier's theorem and the kinetic theory.

3.2. Distribution of a solute between two solvents

(*a*) Distribution law, Ether extraction.

The partition law (only applies when the solute is in the same molecular state in the two solutions, the effect of association of the solute is not required. Solution of liquid in liquid, miscible and immiscible liquids and methods of separation to be treated qualitatively : use of fractional distillation ; solution of solid in liquid, solubility curves, determination of solubility are included The partition or distribution law for the distribution of a solid or liquid between two liquids is similar to Henry's law (deviations not to be considered). Ether extraction : its use in organic chemistry ; it is more economical to use ether in portions (to be explained through numerical examples, using the distribution law with the condition that the solute is in the same molecular state in the two solutions). The use of recrystallisation and fractional crystallisation in the laboratory and in industry.

(*b*) Chromatography.

This may include : (*i*) Column chromatography. (*ii*) Thin-layer chromatography, (*iii*) Paper chromatography, and (*iv*) gas chromatography, a qualitative treatment only is needed with an indication of its use as an analytic tool.

3.3. Colloidal solutions : preparation and properties of colloids, both hydrophillic (e.g., starch or gelatin) and hydrophobic (e.g , S or $As_2S_3$). Precipitation as evidence that colloidal particles are charged.

No treatment of gold number is required. The importance of the large surface area and absorption should also be appreciated.

4. Electrical properties of solutions.

4.1 Application of ionic theory

(a) Solubility product and the common ion effect,

(b) Ostwald's dilution law ; ionic product of water

(c) pH ; (i) pH indicators, (iii) buffer solutions.

Calculations based on the above sub-sections are not required. Ionic equations should be used, where suitable. The law of chemical equilibrium, in terms of molar concentration will need to be first stated (from this law the concept of the solubility product and ionic product for water can be established) ; common-ion effect and its relation to the solubility product should be treated qualitatively without calculations ; the connections between solubility and solubility product and between solubility product and precipitation are to be emphasized in a qualitative manner ; Ostwald's dilution law applied to the case $AB = A^+ + B^+$ should be deduced from the law of chemical equilibrium and the relation between the law and the strength of an acid should be treated qualitatively. The ideas in 7.1(*c*) are to be used to explain, qualitatively, the connection between pH and e.m.f. of a galvanic cell, the concept of weak and strong acids and hydrolysis. The strength of an acid (especially weak acid) increases with dilution.

4.2. Electrode potentials :

(*i*) meaning of the electrode potential,

(*ii*) factors affecting electrode potential,

(*iii*) standard electrode potential,

(*iv*) standard hydrogen electrode,

(*v*) measurement of standard electrode potential,

(*vi*) mechanism of current production in the Voltaic cell,

(*vii*) explanation of the electrochemical series on the basis of electrical properties *i.e.*, standard electrode potential, e.m.f , etc.

## Reaction Kinetics and Chemical Equilibria

5. Chemical kinetics.

(*a*) Qualitative treatment of the dependence of reactions rates on (*i*) concentration of reactants, (*ii*) size of the particle, (*iii*) temperature, (*iv*) presence of a catalyst. The concept of energy barrier. (It is suggested that some experiments may be devised which may deal with the above mentioned factors).

(*b*) Reversible reactions ; dynamic equilibrium.

(*c*) Homogeneous and heterogeneous catalysis.

The presence of the catalyst allows a different mechanism to operate, *i.e.*, a different (usually lower) energy barrier is involved.

(*d*) The concept of equilibrium constants in terms of concentrations or partial pressure to indicate the composition of the equilibrium mixture. The following are examples :

(*i*) the dissociation of dinitrogen tetroxide,

(*ii*) hydrolysis of simple esters,

(*iii*) the contact process for the manufacture of sulphuric acid,

(*iv*) the synthesis of ammonia.

Reference should also be made to solubility product, Ostwald's dilution law, the ionic product of water (see subsection 4.1) in terms of equilibrium constants.

(*e*) Le Chatelier's principle.

Reference should be made to exothermic and endothermic reactions. It should also be emphasized that the change in the volume of an equilibrium constant with temperature demands a corresponding change in the composition of the equilibrium mixture The scope of this section is already suggested in item 3 and 4.1. All treatment is to be qualitative.

(*f*) Chemical reactions and energies.

A qualitative treatment of the following is expected :

(*i*) heat of combustion, (*ii*) heat of formation, (*iii*) heat of reaction, (*iv*) heat of neutralisation, (*v*) heat of solution. Hess's law of constant heat summation and its verification by a simple method.

## SECTION B

**Inorganic Chemistry**

(*a*) General survey of the elements Mg, Al, Ca, Si, P, S, Fe, Cu, Zn, Pb, and their simple familiar compounds.

The general survey should include :

(*i*) Occurrence in nature,

(*ii*) Physical state,

(*iii*) Position in Periodic Table, and discussed on the basis of electronic configuration and relation with neighbouring elements. The resemblance and difference between elements in the same group,

(*iv*) Type of bonding,

(*v*) Nature of oxide, hydroxide, chloride, carbonate, nitrate, sulphate,

(*vi*) Formation of hydride, nitride and carbide. Action of water, air, acid and alkalis.

(*vii*) Gonversion of compounds. Important uses.

Rare earths—with special reference to Lanthanides and Actinides.

Rare gases—with special reference to Helium and Neon (an elementary idea only).

The survey should be based on the Periodic Table. For silicon, treatment should be limited to (*i*) justifying its place in the period (Na to Cl), and (*ii*) illustrating the change of properties within a group, *i.e.*, C, Si and Pb. Opportunity should also be taken to consider the group characteristics as shown by (1) the Halogens and (2) the pairs of elements Na/K, Mg/Ca, C/S. Reference should be made to the location of Fe, Cu, Zn in the Periodic Table. Oxidation and reduction should be discussed in terms of electron transfer.

Silicon, silicates, silicones semi-conductors. Elementary idea of complex compounds. Co-ordination of amines with metals.

(*b*) Laboratory preparation of the important compounds of the above mentioned elements and the manufacture (without technical details) of the compounds and elements used on a large scale e.g., $SO_2$, Fe, Cu, Al, etc.

(*c*) Manufacture of steels, some recent methods, namely, the electric furnace and LD-AC (Linz-Donau) or basic oxygen converter to be dealt with.

7. (*a*) A simple treatment of nuclear fission, e.g., a typical example of the first stage of the fission of $^{235}U$.

Nuclear Equations are required. The general characteristics of nuclear fission (*i*) release of large amounts of energy, (*ii*) the production of lighter nuclei (also radioactive) and other fragments such as helium nuclei and neutrons, is expected.

(*b*) Applications and uses of radio-isotopes such as $^{14}C$ or $^{32}P$. An indication only of the principles of producing radio-isotopes by bombardment is required.

The concept of 'half-life' period is to be appreciated.

## SECTION C

**Organic Chemistry**

Reference should be made to hybridization, sigma and pi bonds.

8. A study of the characteristics properties and reactions of $C{=}C$, $C{-}Hal$, $C{-}OH$, $C{=}O$ and $CHO$, $COOH$, $C{-}NH_2$; illustrated by reference to typical compounds such as : bromoethane, ethyl acetate, ethylamine acetamide, urea, benzene, phenol, aniline, chloroform, chloroethane, formic acid, oxalic acid, glycerol, benzoic acid, glycine, glucose, Optical activity $SN^1$. $SN^2$ reactions, elimination reactions.

Aldol condensation, Meer Ween-pondorff-verely reduction (questions may not be set on this topic.) Cannizzaro reactions. Hofmann reaction. It is expected that basic ideas of reaction mechanism are given.

The laboratory preparation and, where appropriate, the large scale preparation of the following :

Ethylene, acetylene, methyl alcohol, Grignard's reagent, with reference to aldehydes, keytones, amines and acids, acetic acid (vinegar), soaps. Details of purification of these named compounds are not required but the general chemistry of one preparative reaction for each class of compound should be known. The study of a particular compound should also include reference to its alipathic or aromatic character.

Large scale preparation, properties and uses of compounds like $CH_4$, $C_2H_6$, $C_2H_2$ is included.

8.2 Laboratory preparation or other appropriate methods o preparation, properties and uses of the following :

(*a*) ethyl-bromide, di-ethyl ether, acetyl-chloride, ester ethyl-acetate, ethylamine, chloro-benzene, phenol, benzoic acid, nitro-benzene, aniline.

(*b*) acetic-anthydride, acetamide, urea (ammoniacal and potassium cyanate method), oils, soaps, waxes, carbohydrates. Under the carbohydrates, the following are included :

(*i*) Monosaccharides—glucose and fructose,

(*ii*) Disacchrides—sucrose,

(*iii*) Polyasaccharide—starch, cellulose, rayon.

(*c*) Optical activity should be discussed on the following points :

- (*i*) meaning of optical isomerism,
- (*ii*) dextro and laevo rotatory substances,
- (*iii*) use of polarimeter,
- (*iv*) asymmetric carbon atom and enantiomorphs,
- (*v*) optical isomers of lactic and tartaric acids.

9. (*a*) Homologous series, structural isomerism.

(*b*) The principles of addition and condensation polymerisation, illustrated by reference to natural and synthetic polymers, e.g., proteins, polyolefines and synthetic fibres.

Reference should also be made to the effect of chain length and cross linking on the physical properties of polymers.

□

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# PART I

# PHYSICAL CHEMISTRY

# PHYSICAL CHEMISTRY

# Atomic Structure

Dalton (1805) viewed atom as an indivisible entity and, so, without an internal structure. The discovery of cathode rays in 1880, of positive rays in 1886, of X-rays in 1895, and of radioactivity in 1898, however, showed that atom is not the fundamental particle of matter but is made up of smaller sub-atomicparticles.* Of these particles, the proton, the neutron, and the electron are of fundamental importance. Both protons and neutrons are particles of unit weight, but a proton has a unit positive charge and a neutron carries no charge. An electron is a relatively light particle, its weight being about 1/1837 the weight of a proton.

The protons and neutrons are closely packed in an incredibly small volume at the centre of the atom, and make up almost whole of the weight of the atom. The dense body containing the protons and neutrons is called the nucleus of the atom. The nucleus of the atom is positively charged carrying as many units of positive change as the number of protons in it. The electrons are found outside the nucleus in shells or energy levels dispersed at distances that extend up to 100,000 times the diameter of the nucleus. Thus, an atom is mostly 'empty space' around a dense, positively charged nucleus. An atom is electrically neutral. Therefore the number of electrons outside the nucleus is the same as that of the protons in the nucleus. This is the Bohr's model of the structure of the atom.

In the Bohr's model of atomic structure, the electrons are regarded as revolving around the nucleus in *definite* paths, called shells or energy levels, concentric with the nucleus. In the new *wave-mechanical model* of the atom, the electron is a three-dimensional wave surrounding the nucleus of the atom without any definite path.

## 1. Composite Character of Atom

An atom is not a fundamental particle in itself; it has a composite character. There is much experimental evidence to show that atoms are complex systems made up of smaller particles of at least 20 different kinds. Of these, the electron ($e^-$), the proton ($p$), and the neutron ($n$) are the most important. The atoms of all the 103 elements at present known are built up from these three fundamental particles according to a simple plan—successive addition of 1 proton and one or more neutrons in the nucleus and 1 orbital electron. The first element, hydrogen has one proton in the nucleus and one orbital electron. The second element, helium, has two protons (and two neutrons) in the nucleus, and two orbital electrons. Atoms of successive elements are built up in the same way, and the ninety second element, uranium, has 92 protons (and some neutrons) in the nucleus, and 92 orbital electrons. The electron, the proton, and the neutron are, therefore, the building blocks of all atoms.

---

*Since 1912, about 100 fundamental sub-atomic particles have been discovered or postulated.

**1-1. The electron.** When an electric current of high potential is passed through a gas contained at a low pressure (0.03 mm) in a glass tube with a metal electrode sealed in at each end*, rays of bluish light extend from the cathode (negative electrode) in a direction perpendicular to its surface (Fig. 1-1). These rays are called *cathode rays*. When they strike on the wall of the tube opposite, a green fluorescence or glow is produced.

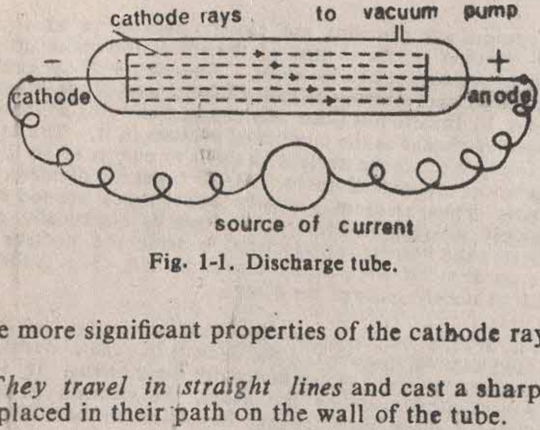

Fig. 1-1. Discharge tube.

Some more significant properties of the cathode rays are—

1. *They travel in straight lines* and cast a sharp shadow of an object placed in their path on the wall of the tube.

2. *They can produce mechanical effects.* Thus, the cathode rays, on striking the blades of a light paddlewheel supported across their path, cause it to rotate. This can happen only if the cathode rays possessed mass and transferred their momentum to the paddles.

3. *They are deflected by magnetic and electrical fields* in a manner which shows that they have a negative charge. Thus, when the discharge tube is placed between two parallel plates, oppositely

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*This type of tube is called a cathode-ray tube or gas discharge tube. It is often called Crookes tube in honour of its inventor.

charged, the cathode rays are repelled by the negative plate and attracted by the positive plate (Fig. 1-2).

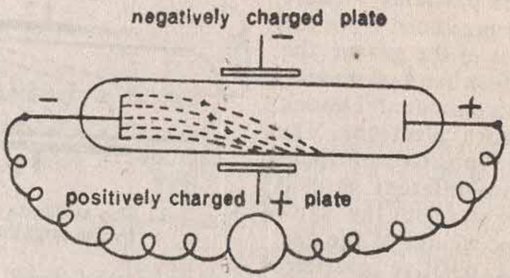

Fig. 1-2. Deflection of cathode rays by an electrical field.

These properties suggest that the cathode rays are streams of *negatively charged particles of matter*. These particles are called *electrons*. In 1897, J.J. Thomson showed that irrespective of he material of the cathode or the gas in the discharge tube, all cathode ray particles have the same charge-mass ratio ($e/m$). Thus he established that electrons from all forms of matter are identical particles. In 1917, Millikan measured the negative charge, $e$, on the electron. This quantity, $1.60 \times 10^{-19}$ coulomb, is the smallest quantity of electricity so far met and is accepted as the unit of electrical charge. From the values of $e/m$ and $e$, the mass of the electron was calculated as $9.11 \times 10^{-28}$ gram. This mass is 1/1840 the mass of a hydrogen atom.

Electrons are also emitted by some metals, *e.g.*, by tungsten when heated (*thermoelectric effect*) and by highly active metals such as potassium, calcium, etc. when exposed to light (*photoelectric effect*). All forms of matter emit electrons under the action of X-rays. Beta rays given off by radioactive substances consist of electrons.

The electrons obtained from all elements by various methods are found to be identical. This proves that *electrons are contained in all atoms*. Recent work has shown that electrons possess not only the properties of particles of matter but the properties of waves as well.

**1-2. The Proton.** In 1886, Goldstein found that the emission of cathode rays is accompanied with the production of another kind of rays, called **positive rays** or **anode rays**. In a discharge tube having a perforated cathode, these rays pass through the pinholes in the cathode in a region behind it. These are deflected in an electrical field in a direction opposite to the deflection of the cathode rays (Fig. 1-3). This shows that these rays are composed of positively charged particles. These particles are produced from the neutral atoms of the gas in the discharge tube when fast moving electrons strike them and knock off one or more electrons. The mass of the positive particles obtained from different gases is different and is about the same as the atomic weight of the gas. The lightest positive particles were obtained from hydrogen and were called **protons**. The electrical charge on a proton is equal in size but opposite in sign to that on the electron. That is, *the proton bears a unit positive charge*. The amount of charge on the positive particles from different gases also varies. The total charge on each particle is either equal to the charge on the proton or some whole number multiple of it. The masses of all positive particles other than proton are also whole number multiples of the mass of the proton. This shows that *proton is the electrically positive unit of atomic structure*. This was conclusively proved by Rutherford in 1919 who showed that protons are produced when nitrogen gas, sodium (vapour), etc. are bombarded with alpha particles.

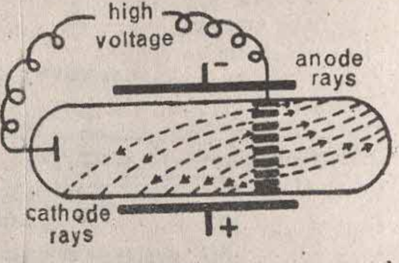

Fig. 1-3. The anode rays are attracted by the negative plate.

The mass of a proton is nearly equal to that of a hydrogen atom (from which it is formed by the loss of an electron of negligible mass).

**1-3. The neutron.** The existence of a neutral, *i.e.*, uncharged particle having a mass of 1 on the atomic weight scale was predicted in 1920 by Rutherford on theoretical considerations.

In 1930, Bothe and Becker found that bombardment of targets of lithium, beryllium, and boron with alpha particles yielded an uncharged radiation with a high penetrating power. They thought that the radiation consisted of gamma rays of very short wavelength. In 1931, Frederic Joliot and his wife Irene Curie found that this radiation ejected high speed protons from a paraffin screen placed in their path. This was a property not characteristic of gamma radiation. In 1932, Chadwick repeated these experiments and calculated that this radiation consisted of particles with no charge and mass equal to that of a proton. This particle was named *neutron*. The neutron is also an essential constituent of all atoms (except protium, $^1_1H$).

The weights and electrical charges of these fundamental units of atomic structure are summarized in Table 1-1.

**Table 1-1.** *Fundamental particles of atomic structure*

| *Particle* | *Symbol* | *Approximate* mass (amu)* | *Electrical charge* |
|---|---|---|---|
| 1. Electron | $e^-$ or $^{0}_{-1}e$ | 0.0 | −1 |
| 2. Proton | $p$ or $^{1}_{1}p$ | 1.0 | +1 |
| 3. Neutron | $n$ or $^{1}_{0}n$ | 1.0 | 0.0 |

## 2. The Nucleus of the Atom

In 1911, Rutherford made an experimental study of the scattering of high-speed* alpha particles (helium ions, $He^{2+}$) by a thin gold foil. These heavy positively charged particles, along with other high energy particles, are given off by radioactive elements. The alpha particles from polonium were directed in a narrow beam at a gold foil 0 003 mm thick (approximately 10,000 atoms across). The direction in which the alpha particles moved was detected by using a movable screen coated with zinc sulphide. The screen was moved in an arc around the centre of the foil (Fig. 1-4). When an alpha particle strikes the screen a point-flash of light is sent out.

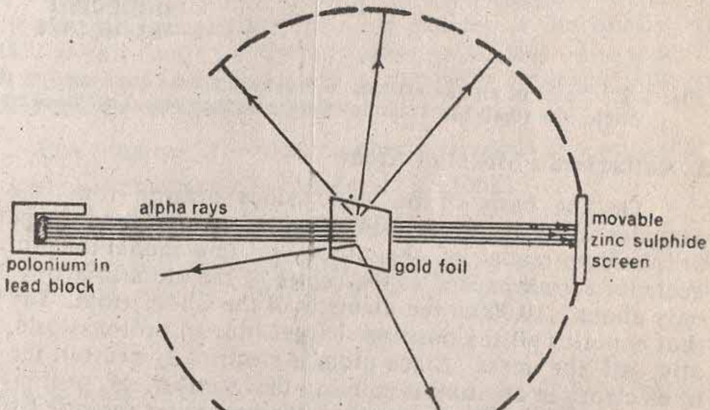

Fig. 1-4. Scattering of $\alpha$-particles by a thin gold foil (entire apparatus is enclosed in an evacuated container).

Three observations were made with regard to the course of the alpha particles. First, most alpha particles passed through the foil without a change in direction as if the foil did not exist. Second, some of the alpha particles were deflected slightly. And third, a few alpha particles were very sharply deflected, sometimes almost straight back. These observations led to the following conclusions :

---

*The atomic mass unit, amu, is defined as 1/12 of the mass of an atom of C-12 isotope, $^{12}_{6}C$. It approximately equals $1.66 \times 10^{-27}$ kg.

**The speed is $2 \times 10^{9}$ cm/sec.

(1) *The atom is largely an empty space* since most of the alpha particles pass undeflected through the gold foil.

(2) *The atom has a heavy, extremely small positively charged body at its centre, called the* **nucleus of the atom**. Owing to its positive charge and high concentration of mass, the nucleus causes the positively charged alpha particles hitting it or approaching it to bounce back or deflect sharply (Fig. 1-5).

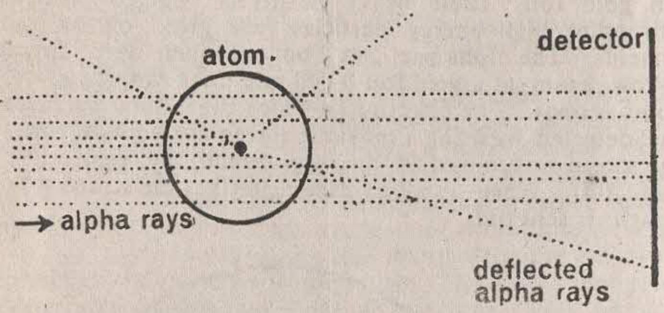

**Fig. 1-5.** Paths of alpha particles through an atom represented by the large circle; the small black circle represents the nucleus of the atom.

### 3. Rutherford's Model of Atom

On the basis of his conclusions drawn from the alpha particles scattering experiment, Rutherford proposed the planetary, or nuclear, model of the atom. In this model the protons and neutrons are all packed at the centre of the atom in a tiny nucleus only about 1/10,000th the diameter of the whole atom. The nucleus thus contains all the positive charges (due to protons) and, essentially, all the mass. Since atom is electrically neutral, the number of electrons in an atom is equal to the number of protons in the nucleus. The electrons occupy the vast outer region of the atom. The limit of space in which the electrons were distributed determined the size of the atom. The electrons were not stationary, as in that case they would be drawn into the positive nucleus by electrostatic attraction, but moved continuously at great speeds around the nucleus in well defined orbits (as the planets do around the sun; hence the term 'planetary model of atom'). The centripetal force of moving electrons balanced the electrostatic attraction*.

---

*If $q_1$ is the charge on the nucleus and $q_2$ is the charge on the orbiting electron whose mass is $m$, velocity is $v$, and orbital radius is $r$, then

$$\underbrace{\frac{q_1 q_2}{r^2}}_{\text{electrostatic attraction}} = \underbrace{\frac{mv^2}{r}}_{\text{cnetripetal force}}$$

This stopped the electrons flying off into space or getting drawn into the nucleus, and thereby held the atom together. The orbiting electrons have little or no effect on the alpha particles.

With its mass, though negligible, and unit negative charge, an electron may possess both kinetic energy (motion energy) and potential energy (energy of position). An electron near the nucleus is strongly attracted by the nucleus and has a low potential energy. An electron farther away from the nucleus is less firmly held and has a high potential energy. An electron also possesses kinetic energy, related to its mass $m$ and velocity $v$ by the relationship K.E $=\frac{1}{2}mv^2$.

**3-1. The atomic number**. The nuclear charge or the number of unit positive charges on the nucleus is called the *atomic number* of the element. It is numerically equal to the number of protons in the nucleus. For example, the nucleus of sodium atom has 11 protons. So, the atomic number of sodium is 11 and the nuclear charge +11. Since the number of protons in any neutral atom must be equal to the number of electrons, the atomic number also gives the number of electrons. Thus, the sodium atom has 11 electrons.

**3-2. The mass number**. The number of protons in an atom plus the number of neutrons is called the *mass number*. Since, the mass of a proton and a neutron are each almost 1 and the mass of the electron is negligible, the mass number is essentially equal to the atomic mass in atomic mass unit (amu). The number of neutrons present in a given atom is obviously equal to the mass number minus the atomic number.

Mass number($A$) = total number of protons and neutrons

Atomic number ($Z$) = number of protons

Mass number − atomic number = number of neutrons

The general notation that is used to represent the mass number and atomic number of a given type of atomic is

$${}^{A}_{Z}\mathrm{E}$$

Where $E$ = the symbol of the element, superscript $A$ = the mass number (in amu), and subscript $Z$ = the atomic number.

**3-3. Isotopes**. An element often has two or more different kinds of atoms which have the same atomic number but different atomic masses or mass numbers. The atoms of the same element having different masses are called *isotopes*. Obviously, the different isotopes of an element have the same number of protons and the same number of electrons, but different number of neutrons. For example, there are two isotopes of chlorine. Each of these isotopes has 17 protons and 17 electrons (atomic number = 17). However, the number of neutrons in one is 18 and in the other 20. The mass number of the isotopes having 18 electrons is 35 and that having 20 electrons is 37. These isotopes are called chlorine-35 (${}^{35}_{17}\mathrm{Cl}$) and chlorine-37 ($^{37}_{17}Cl$) respectively.* Hydrogen has three isotopes. Their atomic number is 1 but their mass numbers are 1,2, and 3. That is, each isotope has 1 proton in the nucleus and 1 electron, but the nucleus in one isotope contains 1 proton only, in the other 1 proton and 1 neutron, and in the third 1 proton and 2 neutrons. These isotopes are symbolized $^{1}_{1}H$, $^{2}_{1}H$, and $^{3}_{1}H$ respectively.

It should be clearly understood that mass number is associated with a single isotope and is not synonymous with atomic weight. The atomic weight of an element is the weighted average of all of its naturally occuring isotopes. Hence, the atomic weights of many elements, unlike the mass numbers of their individual isotopes, are not close to whole numbers.

## 4. Limitations of Rutherford's Nuclear Atom

Rutherford's nuclear model of atom suffers from two major weaknesses:

1. *It does not provide a stable atom.* According to classical physics, a charged particle like electron moving in a curved path around the nucleus would radiate energy. As a result, it would slow down gradually to eventually spiral into the nucleus (Fig. 1-6).

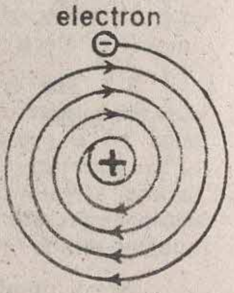

Fig. 1-6. The electron spiralling back into the nucleus in Rutherford's nuclear atom.

2. *It does not explain the origin of the atomic spectra* of the various elements consisting of bright lines separated by dark spaces. Each line in such spectra corresponds to a particular frequency; each dark space corresponds to a frequency range in which no light is emitted. In the Rutherford's model, the electron would gradually lose energy in the from of light (electromagnetic waves). It will, therefore, gradually slow down and spiral into progressively smaller orbits. The wavelength of the emitted light would therefore change in a continuous manner according to the frequency of rotation of electron in the orbit. As such, the continuous energy change would result in a continuous spectrum representing all wavelengths of emitted light.

The foregoing objections against Rutherford's model were met by Niels Bohr who in 1913 proposed a model of atom based on quantum mechanics. This model successfully explained the atomic spectrum of hydrogen.

## 5. Nature of Light and Types of Spectra

Light has been shown to have a particle nature and to be transmitted by a wave motion.

---

*In discussing radioactive elements the atomic number is often deleted from the notation $^{A}_{Z}E$. Thus $^{35}_{17}Cl$ becomes $^{35}Cl$.

**5-1. Light as wave motion.** Light is made up of electromagnetic waves characterized by wavelength, frequency, and velocity. The wavelength $\lambda$ or lambda is the distance from crest to crest in the wave motion (Fig. 1-7). The frequency $\nu$ or nu is the number of waves moving past a point in a unit of time. Since all light waves travel at the same speed, $c$, in a vacuum, as the wavelength increases, the frequency decreases. The relationship between the wavelength, frequency, and speed of an electromagnetic radiation is expressed by the equation

$$c=\lambda\nu$$

The units for the terms in the above equation are usually expressed in centimetres and seconds.

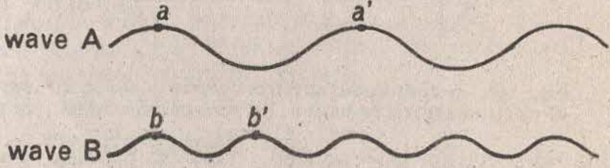

Fig. 1-7. The wavelength a a' of wave A is longer than the wavelength bb' of wave B. If both waves travel at the same velocity (as in the case of light waves), the frequency of wave A is less than the frequency of wave B. That is, for waves travelling at the same velocity, as the wavelength increases, the frequency decreases.

Electromagnetic radiations of various types having different wavelengths or frequencies are now known, *e.g.*, gamma radiation, X-rays, ultraviolet radiation, visible light, infrared radiation, etc. The result obtained when electromagnetic radiations are resolved into their constituent wavelengths or frequencies is called a *spectrum* or *electromagnetic spectrum*. The visible region of the electromagnetic spectrum is a small portion of it to which our eyes respond, the different wavelengths being seen as colours. This region is what is ordinarily called light. Radiations of all wavelengths are detected by instruments called spectroscopes, spectrometers, or spectrographs depending upon the means employed for the detection of the radiation.

**5-2. Light as a form of energy.** Light is a form of energy. This is why the sunlight gives us warmth. Light is emitted as particles, called *photons*, carrying definite quantities or *quanta* (singular, *quantum*) of energy. The energy is not identical for all photons. For examples, photons of violet light have more energy than those of green light which, in turn, have more energy than the photons of red light. According to Planck's quantum theory of light, the energy $E$ of the photon is directly proportional to the frequency $\nu$ of the light (radiation) :

$$E=h\nu$$

where $h$ is a constant called Planck's constant in honour of Max

Planck. That is, higher the frequency (or lower the wavelength), the more energetic are the corresponding photons.

5-3. **Continuous spectrum**. When white light (sunlight or the light from an incandescent solid, *e.g.*, a tungsten ribbon heated to 1000°C) is passed through a prism, a 'rainbow' of colours or a continuous spectrum is produced. This is because the energy of white light is distributed over a continuous range of light frequencies that include the entire visible spectrum. Different frequencies (colours) are bent through different angles by the prism. That is, the different colours in the spectrum correspond to different frequencies. Light energy of the highest frequency (shortest wavelength) is bent most to yield the violet colour at one end of the visible spectrum, and that of the lowest frequency (longest wavelength) is bent least to yield the red colour at the other end. The frequencies lower than the frequency of red light are called *infrared* frequencies. The frequencies higher than the frequency of violet light are called *ultraviolet* frequencies. Thus, a continuous spectrum consists of light (radiation) at all frequencies varying in a continuous manner (Fig. 1-8).

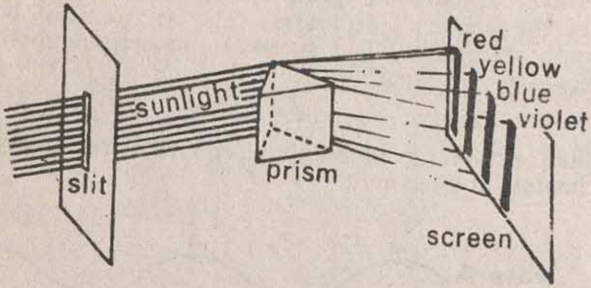

Fig. 1-8. A continuous spectrum is one in which all frequencies of electromagnetic radiation, between certain limits, are present.

5-4. **Line Spectrum**. When atoms in the gaseous state are subjected to an electrical discharge or a high temperature flame, they absorb energy and are said to be excited. The excited atoms emit energy in the form of light radiation. The spectra of light thus emitted shows a series of bright lines* separated by gaps or dark spaces (Fig. 1-9). Each bright line corresponds to a definite frequency emitted; each gap between two adjascent lines corresponds to a frequency range not emitted by the excited atoms.

Fig. 1-9. A line (or atomic spectrum) is one in which only certain frequencies of electromagnetic radiation appear

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*These lines can be recorded on a photographic film in a spectrograph and the wavelength of light producing any particular line can be calculated from its position on the film.

Such spectra in which definite lines may be seen are called *line spectra*. Because line spectra are caused by energy changes taking place within an atom they are also called *atomic spectra*. The light from a mercury vapour lamp or from solid sodium chloride heated in a Bunsen flame provides a line spectrum. Each element produces a line spectrum unlike the spectrum of any other element —a sort of fingerprint !

The fact that the line spectra of elements consist of components of only specific and not all wavelengths or definite energies is significant. It shows that the atoms release energy in certain *fixed* (quantized) amounts. This is possible only if the electrons releasing these particular amounts of energy have certain *fixed* energy levels and are not distributed randomly about the nucleus. The energy will be released in fixed amounts only when an electron jumped from a higher energy level to a lower one; if it *flowed* through, all the possible different values of energy will appear (*i.e.*, a continuous spectrum will result).

## 6. Bohr's Atomic Model

To account for the line spectra of atoms, Niels Bohr, in 1913 proposed a model of atom based on the quantum theory of radiation. The fundamental principle of the quantum theory is that *radiation energy is not absorbed or emitted in continuous amounts but in separate, very minute but definite quantities, called energy quanta*. A quantum of energy, $E$, is not fixed, but is directly proportional to the frequency of radiation $\nu$ which, by its absprotion or emission, causes the change in energy. This relationship is expressed as

$$E=h\nu$$

or, in terms of the wavelength ($\lambda$) of the radiation and the velocity of light ($c$) as

$$E=\frac{hc}{\lambda}\left(\because \nu=\frac{c}{\lambda}\right)$$

where $h$ is Planck's constant, $6{\cdot}62\times10^{-27}$ erg-sec, or $3{\cdot}99\times10^{-13}$ kJ mol$^{-1}$.

**6-1. Main postulates of Bohr's atomic model.** These are—

1. The electrons revolve about the nucleus in certain fixed orbits only. While an electron remains in a given fixed orbit, it does not radiate energy and, therefore, the amount of energy it possesses is unchanged. Such orbits were called **stationary states.** The term stationary state signifies that the energy of the electron is stationary and not changing with time; it does not mean that the electron is stationary.

2. Each orbit or stationary state is characterized by a definite but different amount of energy.* The atoms of each element have a set of special stationary states with a corresponding set of energies. The association of a definite quantity of energy with each orbit has led to the use of the term **energy level** as interchangeable with orbit.

The idea that the electrons in an atom can have only certain characteristic values is often expressed by the statement that the energy of the electrons in *quantized*. Quantization means that the quantity does not vary continuously. Thus, the electrons in an atom can lose or gain energy in discrete amounts only. This can be compared to a ladder on which one can move from one step to another but not part way in between. We can say that the distance covered on a ladder is quantized (this is not so in a moving lift on which the distance varies continuously).

3. An electron may move from one energy level to another. The movement of an electron from a lower energy level to another of higher energy involves absorption of one quantum of energy** Conversely, when an electron moves from a higher energy level to. a lower one, it emits one quantum of radiant energy.

**6-2. Interpretation of atomic spectra.** The electrons in an atom tend to remain in such orbits that the energy of the atom is minimum. The atom is then in its most stable state, and is said to be in the *ground state* By absorption of energy, however, the electrons can jump over to a higher allowed energy level. The atom is then said to be in an *excited state*. The excited electrons do not remain in higher energy levels for long; they lose extra energy by emitting light and move back to a lower energy level. Since only fixed levels of energy exist, only certain energy changes can occur. Thus, if the energy of one stationary state is $E_2$ and that of another with lower energy is $E_1$, an electron passing from the first to the second would cause an energy change of $E_2-E_1$. This energy change represents one quantum of radiant energy, $h\nu$, where $\nu$ is the frequency of the radiation emitted. That is,

$$h\nu=E_2-E_1$$

$$\text{or, } \nu=\frac{E_2-E_1}{h}$$

Thus, the frequency ($\nu$) of the radiation emitted will depend upon the energies of the two levels involved in the transition of electron. Each transition will produce a spectral line of definite frequency (or wavelength).

---

*Here Bohr departed from the atomic models based on classical physics that permitted orbits corresponding to all possible energies.

**In the atom, the negative electron is attracted by the positively charged nucleus. In order to move to a higher energy level, an electron must gain potential energy equal to the work done in overcoming part of the attractive force of the nucleus.

Under the influence of electric discharge or strong heat, the electrons in the individual atoms of a gas are excited to different extent. Each excited electron tends to return to a lower energy level and may stop at any one of the fixed levels on the way back (Fig. 1-10). The greater is the distance between the orbits between which the electron passes backward, the higher is the frequency of the radiation emitted. In any atom, the energies of various orbits have certain fixed values So, the frequencies (or wavelengths) of the emitted radiation can have only some special values characteristic of the atom. Since the electrons do not lose energy in continuous amounts, radiations of all possible frequencies are not produced and the spectrum is discontinuous.

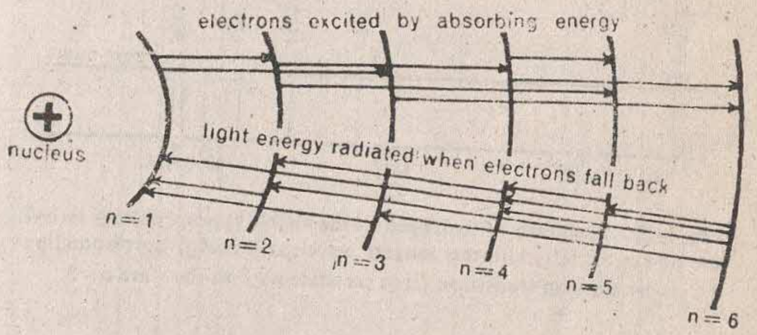
electrons excited by absorbing energy
nucleus
light energy radiated when electrons fall back
n = 1
n = 2
n = 3
n = 4
n = 5
n = 6

Fig. 1-10. Electron transitions responsible for lines in atomic spectra.

## 7. The Hydrogen Spectrum

When a high voltage is passed through hydrogen gas at low pressure in a discharge tube, some of the molecules are dissociated into atoms and violet light is emitted. This light, when passed through a prism, produces a spectrum having distinct lines (Fig. 1-11). The lines in the visible portion of the spectrum can be seen by eye, but those in the ultraviolet and infrared regions are observed photographically.

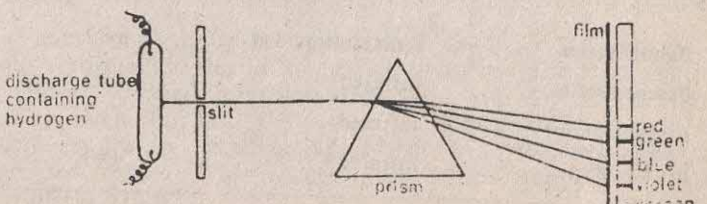

Fig. 1-11. Spectrum of light emitted by hydrogen atoms.

The lines observed in the visible region of the hydrogen spectrum are called the Balmer Series. They consist of a red line, a blue line, a green line, and a series of violet lines increasingly close together at lower wavelengths (Fig. 1-12). These lines are produced by the electrons falling back from the outer, *i e.*, higher energy levels to the second energy level (n=2). The orbits or energy levels are numbered 1,2,3,4..., counting outward from the nucleus.* This number is called the principal quantum number, which is given the symbol *n*.

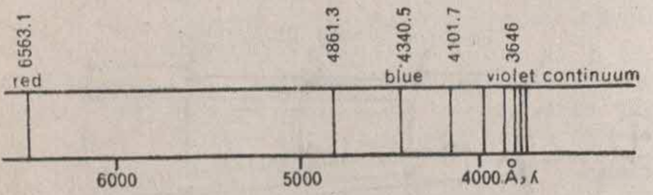

**Fig. 1-12.** Spectrum of hydrogen in the visible region (Balmer series); the line at the left, with the longest wavelength is $H_\alpha$ corresponding to he electron transition from the state n = 3 to the state n = 2.

There are in all five series of spectral lines in the hydrogen spectrum (Table 1-2, Fig. 1-13). These are called the Lyman series, the Balmer series, the Paschen series, the Brackett series, and the Pfund series.

**Table 1-2** *Series of lines in the hydrogen spectrum*

| *Name of series* | *Regions of spectrum* | *Resulting from electrons dropping to energy level* |
|---|---|---|
| 1. Lyman series | ultraviolet | n = 1 (the lowest or ground state) |
| 2. Balmer series | visible/ultraviolet | n = 2 |
| 3. Paschen series | infrared | n = 3 |
| 4. Brackett series | infrared | n = 4 |
| 5. Pfund series | infrared | n = 5 |

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*The orbits are sometimes denoted by the letters K,L,M,N, etc, corresponding to n = 1,2,3,4, etc

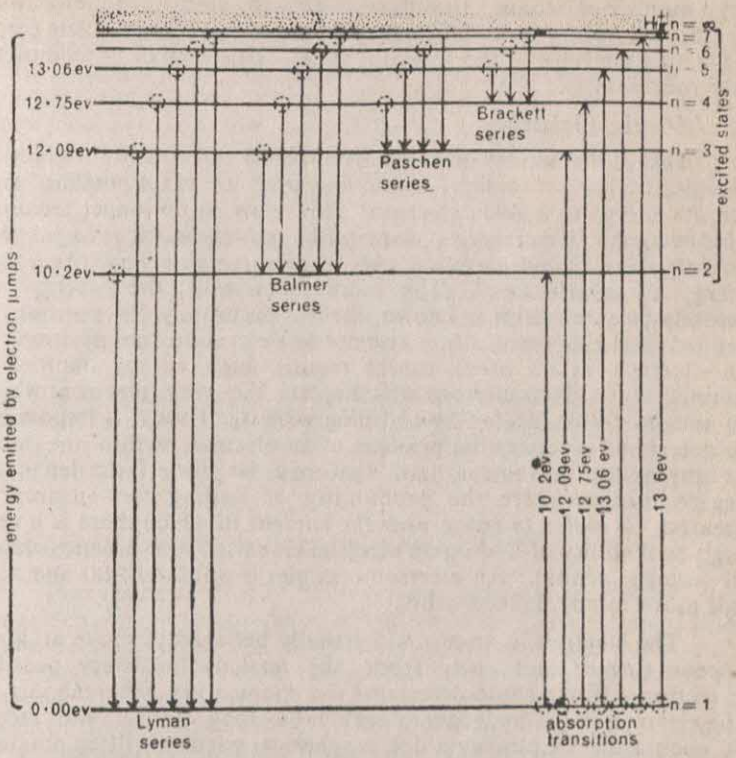


**Fig. 1-13. Series of spectral lines in the emission spectrum of hydrogen (Pfund series not shown; The numbers $n=1,2,3......$ represent various energy levels).**

As in the case of Balmer series, the spectral lines in all other series converge towards higher frequencies (lower wavelengths), *i.e.*, crowd closer together until the continuum or limit is reached. The convergence limit of the Lyman series, as also of the other series, approaches the ionization energy of hydrogen electron which is the energy necessary to completely pull it away from the atom. This fact suggests that the electron can exist in certain fixed distance energy levels and not randomly about the nucleus.

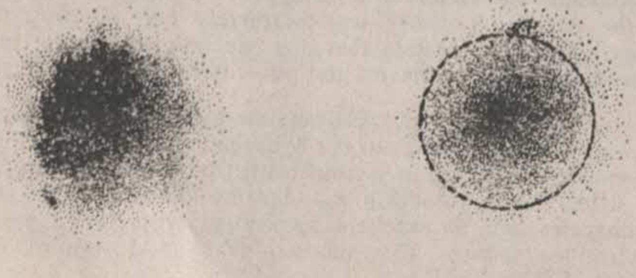
From Bohr's model it is possible to calculate the energies of various stationary states in the hydrogen atom. The frequencies of the radiation emitted in various transitions can also be calculated by using the relationship $E_2-E_1=h\nu$. The calculated values of frequencies are in excellent agreement with the experimentally determined values This success gave good support to Bohr's model of the atom.

Though the hydrogen atom consists of only one electron, the spectrum of hydrogen atoms shows a large number of lines. This is because even a very small quantity of hydrogen yields a very large number of atoms In different excited atoms, the electrons go through every possible transition involving energy levels from the ionization limit to the ground state. This makes a complete spectrum possible.

## 8. Atomic Orbitals

The Bohr model has electron orbits of definite radii and energies. Thus, it assigns simultaneously an exact position and definite energy to a given electron. This view is no longer tenable. According to *Heisenberg's uncertainty principle*, "*it is impossible to determine simultaneously the exact position and the exact energy of an electron*". The more accurately the energy or velocity of an electron is known, the less accurately its position is defined, and *vice versa* Any attempt to determine the position of an electron in an atom would require high energy photons to illuminate it. Such photons will displace the very electron which is sought to be located by colliding with it. Thus it is impossible to determine precisely the position of an electron within the atom at any given movement. All that can be done is to define the region in space where the probability of finding the electron is greatest. *A region in space near the nucleus* in which there is a very high probability of finding an electron is called an *atomic orbital* or simply orbital. An electron occupies a whole orbital and does not move in any defined orbit.

The electron in an atom is actually believed to move at great speeds toward and away from the nucleus in every possible direction. If one could determine the momentary whereabouts of the electron in the hydrogen atom over a long period and record it each time by placing a dot, a spherical pattern will be obtained (Fig. 1-14 a). This pattern is called an *electron cloud* diagram. It is most dense near the nucleus and has no distinct edge. That is, at one time the electron may be at the nucleus and at another time far away from the nucleus. Commonly, instead of charge clouds, their boundaries are drawn enclosing a region in which the probability of finding the electron is greater than ninety five per cent (Fig. 1-14 b). The distance of this boundary from the nucleus



(a) (b)

Fig. 1-14. Representations of an electron cloud.

is the radius of maximum probability of electron presence. It is 0·53 Å, the same as calculated from the Bohr's model. But while Bohr thought that the electron of hydrogen was *always* at that distance, the orbital concept indicates that the electron is *most likely* at the distance. Or, there is a greater probability that the electron is at a distance of 0·53 Å from the nucleus than at any other distance.

An electron in a given orbital is associated with a definite energy. The energy is lower if the orbital is close to the nucleus as the electron is more strongly attracted. The change in energy from one orbital to another is not continuous, but quantized. *i.e.*, the change occurs jumpwise in definite portions or quanta.

It is found that an orbital can accomodate no more than two electrons (see Sec. 12), In other words, an orbital may contain no electrons, or it may contain one or two electrons and is said to be unoccupied, singly occupied, or doubly occupied respectively.

## 9. Energy Levels, Sublevels, and Orbitals

Every spectral line of hydrogen has been found, under great magnification, to be composed of two or more closely spaced lines. Since each spectral line corresponds to the movement of electron from one energy level to another, this observation points to the presence of extra, closely spaced energy levels within the energy levels of the hydrogen atom. When the excited atoms are placed in a magnetic field, some single lines are split into closely spaced clusters (Zeeman effect). Obviously, new energy levels are created in the presence of a magnetic field. All this experimental evidence indicates that *each energy level is composed of one or more sub-levels, each having a slightly different energy, and each sublevel is composed of one or more orbits.*

**9-1. Energy levels.** The non-radiating orbits of electrons around the nucleus are called energy levels or shells. Each energy level is specified by a principal quantum number, $n$, which has whole number values 1,2,3,......outward from the nucleus. In the older notation, the energy levels were lettered K,L,M,......., etc. (Fig. 1-15). The energy levels increase in energy as they increase in distance from the nucleus. That is, the nearer the electron is to the nucleus, the less energy it has as it is more strongly attracted by the nucleus; the further away it is, the more energy it has. As an electron absorbs energy it goes from one energy level to another, and not partway between. That is, the energy of the electrons in various energy levels is quantized.

The maximum number of electrons in each energy level is $2n^2$ where $n$ is the the number of the energy level. Therefore, in the first energy level ($n=1$) the maximum is $2\times1^2=2$, in the second energy level ($n=2$) the maximum is $2\times2^2=8$, in the third ($n=3$) it is $2\times3^2=8$, and so forth.

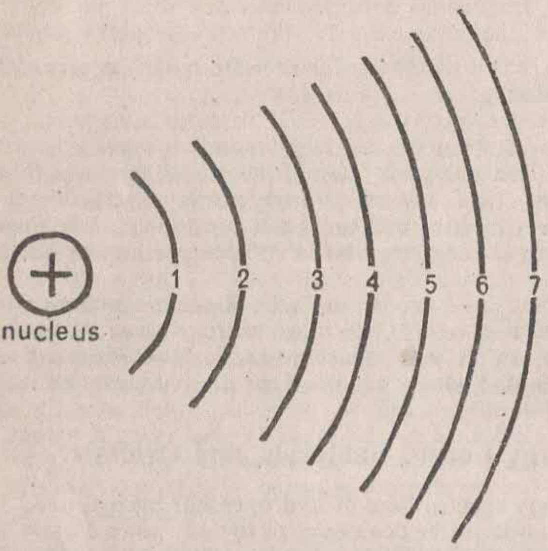


Fig. 1-15. Energy levels.

**9-2. Energy sublevels.** Each main energy level is divided into sublevels or subshells containing electrons that have slightly different energies. *The number of sublevels in an energy level is equal to the number of the energy level.* The first energy level has only one sublevel, called 1*s*; the second energy level has two sublevels, called 2*s* and 2*p*; the third energy level has three sublevels, called 3*s*, 3*p*, and 3*d*; and the fourth energy level has four sublevels, called 4*s*, 4*p*. 43*d*, and 4*f*. In their ground states (in which the electrons occupy energy levels nearest the nucleus), atoms have only these four sublevels of energy, *s*, *p*, *d*, and *f**. On an average, an *s* electron of an energy level approaches closer to the nucleus than a *p* electron, *a p* electron closer to the nucleus than a *d* electron, and so on. Thus, the energies of the sublevels of a given energy level vary in the order $s<p<d<f$.

Each type of sublevel has a maximum number of electrons that it can hold. An *s* sublevel can hold a maximum of 2 electrons, a *p* sublevel can hold a maximum of 6 electrons, a *d* sublevel can hold a maximum of 10 electrons, and an *f* sublevel can hold a maximum of 14 electrons.

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*The letters *s*, *p*, *d*, and *f* come from the spectroscopic terms sharp, principal, diffuse, and fundamental, which were used to describe the lines in the atomic spectra.

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**9-3. Orbitals.** Each energy sublevel or subshell is composed of one or more orbitals. The set of orbitals that make up a particular sublevel are all of equal energy, except in the presence of an external magnetic field. An *s* sublevel has one *s* orbital, a *p* sublevel consists of a set of three *p* orbitals, a *d* sublevel consists of a set of five *d* orbitals, and an *f* sublevel consists of a set of seven *f* orbitals. Each orbital can accomodate a maximum of two electrons. Thus, the maximum number of electrons is 2 in an *s* sublevel with one orbital, 6 in a *p* sublevels with three orbitals, 10 in a *d* sublevel of five orbitals, and 14 in an *f* sublevel with seven orbitals.

It is obvious that the electrons actually occupy orbitals rather than shells. When a principal shell has all its orbitals occupied by two electrons of opposite spins, it is said to be completely filled.

## 10. Quantum Numbers

An electron within an atom is specified by four quantum numbers : (1) the principal quantum nember, (2) the subsidiary or azimuthal quantum number, (3) the magnetic quantum number, and (4) the spin quantum number.*

*1. The principal quantum number*, $n$, can have any positive integral value from one on— 1,2,3,4,......etc. *The value of n specifies the main energy level and is related to the size of the electron cloud.* Increasing values of $n$ correspond to incseasing size of the electron cloud and, therefore, to increasing distance from the nucleus and increasing energy for the electron.

The orbitals having the same value of $n$ constitute a particular main energy level or electron shell.

*2. The subsidiary quantum number*, $l$, has numerical values related to $n$; $l$ can have any integral value from 0 to $(n-1)$ inclusive. When $n=1$, $l$ can have only the value of 0; when $n=2$, $l$ can be 0 and 1; when $n=3$, $l$ can be 0,1, and 2; and so on. *The value of l describes a particular sublevel within a given main energy level and determines the shape of the electron cloud.* For $l=0$, the electron cloud is spherical and for $l=1$, the electron cloud is dumbbell-shaped. The sublevels with the values of $l=0$, 1, 2, and 3 are designated by letters *s*, *p*, *d*, and *f* respectively. In any given energy level, the energy of the sublevels increases in the order $s<p<d<f$.

Since for any value of $n$ there can be $n$ different values for $l$ (0 to $n-1$ inclusive), *the number of sublevels or subshells in a given energy level is equal to its principal quantum numbers, n.* The first energy level contains only one sublevel, the *s* sublevel, the second energy level contains two sublevels, *s* and *p*, the third energy level

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*The first three quantum numbers come from the allowed solutions to a complex equation, called the *Schrodinger wave equation*. The fourth quantum number arises from other considerations.

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has three sublevels, *s*, *p*, and *d*; and the fourth energy level has four sublevels, *s*, *p*, *d*, and *f*.

**Table 1-3.** *Sublevels for first four energy levels*

| *Principal quantum number, n* | *Number of sublevels* | *Subsidiary quantum numbers (0 to n—l)* | *Notation for sublevel* |
|---|---|---|---|
| 1 | 1 | 0 | $1s$ |
| 2 | 2 | 0, 1 | $1s$, $2p$ |
| 3 | 3 | 0, 1, 2 | $3s$, $3p$, $3d$ |
| 4 | 4 | 0, 1, 2, 3 | $4s$, $4p$, $4d$, $4f$ |

*3. The magnetic quantum number*, $m$, also has integral values which depend on the value of $l$. This can have any integral value from $-l$ to $+l$, including zero. Thus there are $(2l+1)$ values for $m$ for any given value of $l$. For each value of $m$ there is an electron orbital in the energy sublevel. So the total number of different orbitals within a given sublevel (designated by the value of $l$) is $2l+1$.

*The values of m specify the orientations in space for an electron cloud.* When $l=0$ (*s* sublevel), $m$ has only one value 0; therefore there is only one orientation in space—spherical—or a single orbital. This orbital is called an *s* orbital. When $l=1$, (*p* sublevel), $m$ can be $-1$, 0, and $+1$; therefore there are three orientations in space or three orbitals in the sublevel. These orbitals are called *p* orbitals. When $l=2$ (*d* sublevel), m can be $-2$, $-1$, 0, $+1$, and $+2$; there are five orientations in space or five *d* orbitals in the sublevel. When $l=3$ (*f* sublevel), $m$ can be $-3$, $-2$, $-1$, 0, $+1$, $+2$, and $+3$; therefore there are seven orientations in space or seven *d* orbitals in the sublevel.

**Table 1-4.** *Number of orbitals in sublevels*

| *Subsidiary quantum number, l* | *Notations for sublevel* | *Magnetic quantum number, m (—l to + l)* | *Number of orbitals in the sublevel* |
|---|---|---|---|
| 0 | *s* | 0 | 1 |
| 1 | *p* | $-1, 0, +1$ | 3 |
| 2 | *d* | $-2, -1, 0, +1, +2$ | 5 |
| 3 | *f* | $-3, -2, -1, 0, +1, +2, +3$ | 7 |

All orbitals of a given sublevel (same value of $l$ but different values of $m$) have the same energy because they differ only in direction, not in size or shape of their distributions. When an atom interacts with other atoms or with an external magnetic or electrical field, the spatial arrangement and energy by the orbitals is slightly changed.*

---

*Owing to its charge, a moving electron itself creates a magnetic field, the direction of which is at right angle to the plane of the orbit (compare with the magnetic field produced by a current in a coil of wire). In an external magnetic field, the magnetic fields of the electrons take up definite orientations with respect to the former. This introduces small changes in the energy of the orbitals of the sublevel which had identical energy in the absence of external magnetic field (Zeeman effect).

*4. The spin quantum number*, s, describes the *spin of the electron*. In some cases it was found that spectral lines were split still further into two lines (doublet). This was explained by assuming that an electron, while moving in an orbit, spins on its axis like a top. The energy of the spin is also quantized, and can have either of the two values : $+h/2\pi$ and $-h/2\pi$. The direction of the electron spin is specified by the spin quantum number, $s$. It has only two values $+\frac{1}{2}$ and $-\frac{1}{2}$ corresponding to clockwise and anticlockwise spin respectively (Fig. 1-16).

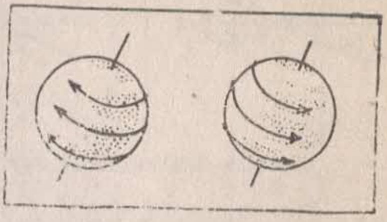

Fig. 1-16. Electron Spinning in a clockwise motion (left) and in an anticlockwise motion (right).

## 11. Size, Shapes, and Orientations of Orbitals

The size, shapes, and orientation in space of electron orbitals are related to values of $n$, $l$, and $m$, respectively. An $s$ orbital ($l=0$), regardless of the values of $n$, has the shape of a sphere surrounding the nucleus. Thus, it has only one possible orientation ($m=0$) (Fig. 1-17). The probability of finding the electron is maximum within a certain distance from the nucleus which is taken as the radius of the $s$ orbital. The size of the orbital increases with the increasing value of $n$. Thus, the 2$s$ orbital ($n=2$) is larger than the 1$s$ orbital ($n=1$) but smaller than the 3$s$ orbital. The 2$s$ orbital is thus a larger sphere concentric with and encompassing the much smaller 1$s$ orbital (Fig. 1-18). The 1$s$ and 2$s$ orbitals are separated by a zone of zero electron density.

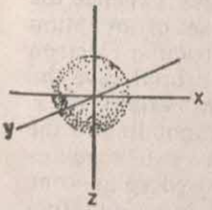

Fig. 1-17. The 1 s orbital.

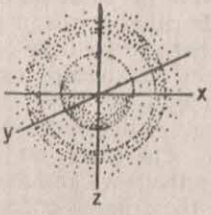

Fig. 1-18. The 1 s and 2 s orbitals.

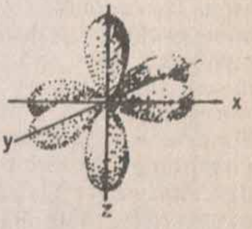

Fig. 1-19. The three 3 p orbitals.

The $p$ orbitals ($l=1$) have the shape of dumb-bells concentric with the nucleus, and have three orientations ($m=-1, 0, +1$). The three p orbitals are located at right angles to each other in space along $x$, $y$, and z axes. The corresponding orbitals are termed $p_x$, $p_y$, and $p_z$ orbitals (Fig. 1-20). Note that in the $p$ orbitals there is an area of zero probability density along the axis that contains the nucleus. However, the electron clouds that make up the two parts of the dumbbell represent the region in space where the pair of electrons of the orbital will be found 95 per cent of the time. Do not think that each part of the dumbbell has one electron out of the pair of electrons.

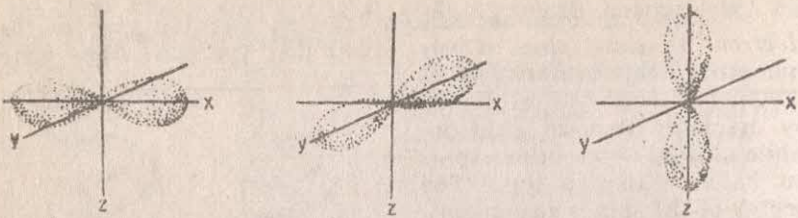

Fig. 1-20. (left) $p_x$ orbital; (centre) $p_y$ orbital; (right) $p_z$ orbital.

The shapes of *d* and *f* orbitals are more complicated, and their representation is omitted here. It may be noted, however, that a set of *p* orbitals taken together gives nearly a spherical shape (Fig. 1-19), and the same is true for a set of *d* orbitals and f orbitals. That is, when each orbital of a sublevel is equally occupied by one or two electrons, the electron cloud for the whole sublevel is spherical.

Keep in mind that the shapes of orbitals shown in the foregoing figures represent three-dimensional digrams and the axes shown are not part of the atom; they are simply a notation used in discussing orbitals and electron clouds.

## 12. Pauli Exclusion Principle

Pauli exclusion principle is an important rule that governs the occupation of orbitals by electrons in many-electron atoms. It states that *no two electrons in an atom can have all four quantum numbers the same*. If one electron in an atom has a particular set of the four quantum numbers *n*, *l*, *m*, and *s*, all other electrons in that atom are *excluded* from having the same set of values (whence the name exclusion principle). In other words, a given set of quantum numbers *n*, *l*, *m*, and *s* can characterize only one particular electron in an atom. Since the electrons occupying an orbital have the same values of *n*, *l*, and *m*, they must have different values of *s*. However, *s* has only two values $+\frac{1}{2}$ and $-\frac{1}{2}$ corresponding to the direction of the electron spin. Therefore, an orbital can accomodate not more than two electrons which have opposed spins—one having the value $+\frac{1}{2}$ and the other $-\frac{1}{2}$ for the spin quantum number. The two electrons with opposed spins in an orbital are said to be *paired*; these are represented by a pair of opposed arrows ⇅. When an orbital has only one electron in it, we say that the electron is *unpaired*.

By applying Pauli exclusion principle and permutating the quantum numbers, the maximum number of electrons which can be contained in only energy level can be easily calculated. This is illustrated in Table 1-5 (page 25) for the first three energy levels. It may be noted that as one progresses from one main energy level to the next higher one, a new sublevel is added in addition to those existing in the preceding main energy level. Thus, in

Table 1-5

*Maximum number of electrons contained in the first three energy levels and sub-levels*

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Principal quantum number, *n*, | 1 | 2 | | | | 3 | | | | | | | | |
| Azumuthal quantam number, *l* | 0 | 0 | 1 | | | 0 | 1 | | | 2 | | | | |
| Magnetic quantum number, *m* | 0 | 0 | —1 | 0 | +1 | 0 | —1 | 0 | +1 | —2 | —1 | 0 | +1 | +2 |
| Spin quantum number, *s* | $+\frac{1}{2}$<br>$-\frac{1}{2}$ | $+\frac{1}{2}$<br>$-\frac{1}{2}$ | $+\frac{1}{2}$<br>$-\frac{1}{2}$ | $+\frac{1}{2}$<br>$-\frac{1}{2}$ | $+\frac{1}{2}$<br>$-\frac{1}{2}$ | $+\frac{1}{2}$<br>$-\frac{1}{2}$ | $+\frac{1}{2}$<br>$-\frac{1}{2}$ | $+\frac{1}{2}$<br>$-\frac{1}{2}$ | $+\frac{1}{2}$<br>$-\frac{1}{2}$ | $+\frac{1}{2}$<br>$-\frac{1}{2}$ | $+\frac{1}{2}$<br>$-\frac{1}{2}$ | $+\frac{1}{2}$<br>$-\frac{1}{2}$ | $+\frac{1}{2}$<br>$-\frac{1}{2}$ | $+\frac{1}{2}$<br>$-\frac{1}{2}$ |
| Orbitals | 1*s* | 2*s* | $2p_x$ | $2p_y$ | $2p_z$ | 3*s* | $3p_x$ | $3p_y$ | $3p_z$ | —five *d* orbitals | | | | |
| Maximum number of electrons in an energy sub-level | 2 | 2 | 6 | | | 2 | 6 | | | 10 | | | | |
| Maximum number of electrons in an energy level ($2n^2$) | 2 | 8 | | | | 18 | | | | | | | | |

addition to the sublevels in the third energy level ($n=3$), the fourth energy level ($n=4$) has a new $4f$ sub-level ($l=3$). This sublevel will have seven orbitals with quantum numbers $-3, -2, -1, 0, +1, +2$, and $+3$. These seven orbitals will accomodate a total of 14 electrons. So, the maximum number of electrons in the fourth energy level will be 18 (as in the third energy level) plus 14, *i.e.*, 32.

## 13. Relative Energies of Energy Sublevels

Within each energy level, the *s* sublevel is of lower energy than the *p* sublevel, which is of lower energy than the *d* sublevel, and so on. That is, the energies of the sublevels in an energy level vary in the order $s<p<d<f$. This is because of the differences in angular momentum of the electrons in these sublevels. Angular momentum increases with the value of *l*, *i.e.*, in the order *s*, *p*, *d*, *f*. As a result an *s* electron approaches closer to the nucleus than a *p* electron, a *p* electron closer to the nucleus than a *d* electron, and so on causing small energy differences. However, the spread in energy between the sublevels of a main energy level is wide enough to cause overlap between the sublevels of different energy levels. Such overlap starts beyond the $3p$ sublevel. The three sublevels of the third main energy level ($n=3$) differ in energies in such amounts that the $3d$ sublevel has higher energy than the $4s$ sublevel. The differences in the energy of various sublevels are of

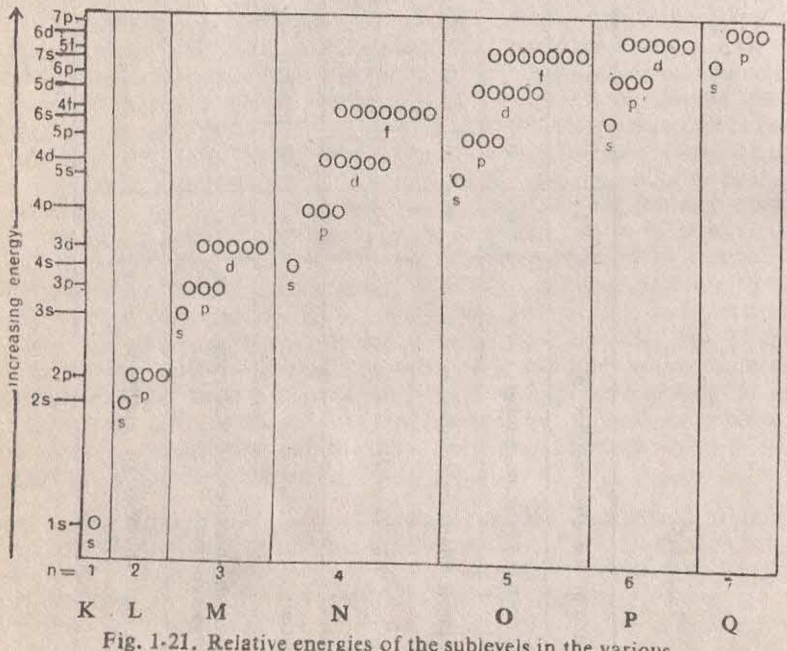

Fig. 1·21. Relative energies of the sublevels in the various energy levels (up to $n=7$).

significance in determining the order in which electrons occupy the orbitals in building up atmos.

The relative energies of the sublevels in the various energy levels increase in the order $1s$, $2s$, $2p$, $3s$, $3p$, $4s$, $3d$, $4p$, $5s$, $4d$, $5p$, $6s$, $4f$, $5d$, $6p$, $7s$, $5f$, $6d$. $7p$ (Fig. 1-21). It must kept in mind that the various orbitals within any given sublevel are all of equal energy.

## 14. Representation of Electronic Configuration

The ground state electronic configurations of atoms, *i.e.*, the distributions of electrons in energy levels and sublevels are represented by the notation

$$nl^x$$

where $n$ is the principal quantum number of the energy level, indicated by the appropriate number 1, 2, 3,......; $l$ specifies the sublevel by the appropriate letter $s$, $p$, $d$, or $f$ (corresponding to $l$=0, 1, 2, and 3); and $x$ is the number of electrons in the sublevel. For example, the electronic configuration of nitrogen is represented as $1s^2$, $2s^2$ $2p^3$. This signifies that a nitrogen atom has 2 electrons in the $s$ sublevel of the first energy level, 2 electrons in the $s$ sublevel of the second energy level, and 3 electrons in the $p$ sublevel of the second energy level. The three electrons in the $2p$ level of nitrogen atom singly occupy the three $p$ orbitals. This detail of electron distribution can be represented as $1s^2$, $2s^2$ $2p_x^1$ $2p_y^1$ $2p_z^1$, the subscripts $x$, $y$, and $z$ specifying particular 2p orbitals. Such details are usually given only for the electrons of the valence shells.

Electronic configuration of a few more atoms in the $nl^x$ notation are given below for illustration :

| *Element* | *At. no.* | *Electronic configuration* |
|---|---|---|
| **Sodium** | 11 | $1s^2$, $2s^2$ $2p^6$, $3s^1$ |
| **Sulpher** | 16 | $1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^4$ |
| **Chlorine** | 17 | $1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^5$ |
| **Silver** | 47 | $1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^6$ $3d^{10}$, $4s^2$ $4p^6$ $4d^{10}$, $5s^1$ |

## 15. Build-up of Atoms

When atoms are in their ground state, the electrons occupy the lowest energy levels available. The simplest element hydrogen has one proton in the nulceus and one electron in the $1s$ orbital. Atoms of elements following hydrogen may be regarded to form by the addition of one electron to an orbital and of one proton and one or more neutrons to the nucleus. The addition of successive electrons in the build-up of atoms in governed by the following rules :

1. *The electrons occupy the orbitals in order of increasing energy* (Aufbau* Principle). That is the added electron enters an

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*Aufbau (आफबाओ) is a German term meaning construction or build-up orbital in the sublevel of lowest energy thus giving minimum potential energy or maximum stability to the atom. As a working rule, the new electron enters an orbital in the sublevel for which the value $n+l$ is minimum. If the value is identical for two or more sublevels, the new electron enters an orbital in the sublevel for which $n$ is the smallest value. Fig. 1-22 is a useful guide to the order of increasing energy of the various sublevels. Note that this order is the same as given in Sec. 13, page 27.

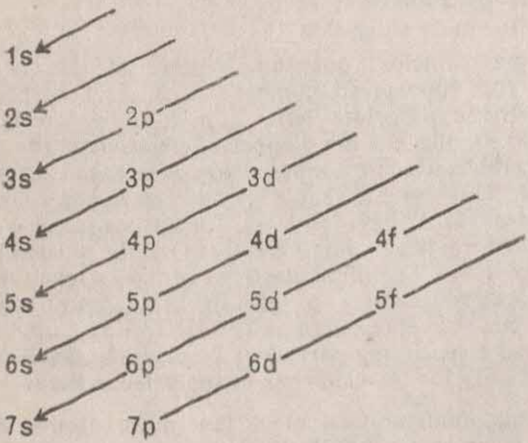

Fig. 1-22. Electron sublevels in order of increasing energy.

2. *An orbital can be occupied by not more than two electrons (Pauli exclusion principle).*

3. *The electron occupies a vaccant orbital in preference to pairing in a singly occupied orbital in the same sublevel (Hund's rule of maximum multiplicity).* That is, if two or more orbitals are available in the same sublevel (these orbitals have equal energy), the electron will enter an orbital which is not already occupied by an electron. This is because a lower energy state results if two electrons are in separate orbitals than if they occupy the same orbital in which case the electrostatic repulsion is high.

Hund's rule is illustrated in Table 1-6 for the first ten elements.

**Table 1-6** *Filling of orbitals in elements of atomic numbers 1 to 10*

| *Element* | *At. No.* (*=no. of electrons*) | *Orbital* | | | | | *Remark* |
|---|---|---|---|---|---|---|---|
| | | *n=1* | *n=2* | | | | |
| | | *1s* | *2s* | $2p_x$ | $2p_y$ | $2p_z$ | |
| H | 1 | ↑ | | | | | The electron occupies 1*s* orbital. |
| He | 2 | ↑↓ | | | | | second electron also enters 1*s* orbital. |
| Li | 3 | ↑↓ | ↑ | | | | New electrons enters 2*s* orbital. |
| Be | 4 | ↑↓ | ↑↓ | | | | New electrons pairs with a 2*s* eleetron. |
| B | 5 | ↑↓ | ↑↓ | ↑ | | | New electrons enters a *p* orbital. |
| C | 6 | ↑↓ | ↑↓ | ↑ | ↑ | | New electron enters another vacant *p* orbital. |
| N | 7 | ↑↓ | ↑↓ | ↑ | ↑ | ↑ | New electron enters still another vacant *p* orbital, |
| O | 8 | ↑↓ | ↑↓ | ↑↓ | ↑ | ↑ | New electron pairs with a *p* electron in orbital as no vacant *p* orbital is available. |
| F | 9 | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑ | |
| Ne | 10 | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | |

*Note.* Electron distribution in orbitals is often shown by electron diagrams in which the sublevels are represented by boxes, one box for each orbital, and the electrons with arrows. This is illustrated in the orbital diagrams of nitrogen and oxygen given below:

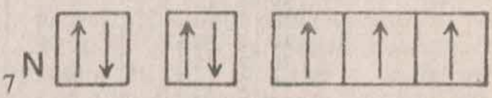

Fig. 1-23. Orbital diagram of nitrogen.

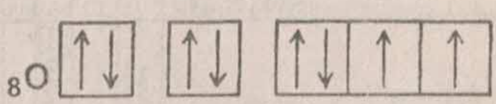

Fig. 1-24. Orbital diagram of oxygen.

4. *Orbitals in an energy level tend to become fully filled or half filled with electrons.* This is because the fully filled and half-filled orbitals have lower energy and, therefore, more stability. Thus, chromium and copper take up $d^5$ and $d^{10}$ configuration respectively and not the $d^4$ and $d^9$ configurations.

Chromium (at. no. 24), in accordance with the first three rules for occupation of orbitals by electrons, should have the configuration $1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^6$ $3d^4$, $4s^2$. However, the actual configuration is $1s^2$. $2s^2$. $2p^6$. $3s^2$ $3p^6$ $3d^5$. $4s^1$ because one of the 4s orbital electrons moves into the vacant *d* orbital to make a more

**Table 1-7** *Electronic configurations of atoms*
(atomic number 1—54)

| *Shell*→ | 1 | 2 | | 3 | | | 4 | | | | 5 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Sub-shell*→ | *1s* | *2s* | *2p* | *3s* | *3p* | *3d* | *4s* | *4p* | *4d* | *4f* | *5s* | *5p* | *5d* | |
| *Element* | | | | | | | | | | | | | | |
| 1 H | 1 | | | | | | | | | | | | | |
| 2 He | 2 | | | | | | | | | | | | | 1*s* full |
| 3 Li | 2 | 1 | | | | | | | | | | | | |
| 4 Be | 2 | 2 | | | | | | | | | | | | 2*s* full |
| 5 B | 2 | 2 | 1 | | | | | | | | | | | |
| 6 C | 2 | 2 | 2 | | | | | | | | | | | |
| 7 N | 2 | 2 | 3 | | | | | | | | | | | |
| 8 O | 2 | 2 | 4 | | | | | | | | | | | 2*p* full |
| 9 F | 2 | 2 | 5 | | | | | | | | | | | |
| 10 Ne | 2 | 2 | 6 | | | | | | | | | | | |
| 11 Na | Neon Core of 10 electrons | | | 1 | | | | | | | | | | |
| 12 Mg | | | | 2 | | | | | | | | | | 3*s* full |
| 13 Al | | | | 2 | 1 | | | | | | | | | |
| 14 Si | | | | 2 | 2 | | | | | | | | | |
| 15 P | | | | 2 | 3 | | | | | | | | | |
| 16 S | | | | 2 | 4 | | | | | | | | | 3*p* full |
| 17 Cl | | | | 2 | 5 | | | | | | | | | |
| 18 A | | | | 2 | 6 | | | | | | | | | |
| 19 K | Argon Core of 18 electrons | | | | | | 1 | | | | | | | |
| 20 Ca | | | | | | | 2 | | | | | | | 4 *s* full |
| 21 Sc | | | | | | 1 | 2 | | | | | | | |
| 22 Ti | | | | | | 2 | 2 | | | | | | | |
| 23 V | | | | | | 3 | 2 | | | | | | | |
| 24 Cr | | | | | | 4 | 1 | | | | | | | |
| 25 Mn | | | | | | 5 | 2 | | | | | | | |
| 26 Fe | | | | | | 6 | 2 | | | | | | | 3*d* full |
| 27 Co | | | | | | 7 | 2 | | | | | | | |
| 28 Ni | | | | | | 8 | 2 | | | | | | | |
| 29 Cu | | | | | | 10 | 1 | | | | | | | |
| 30 Zn | | | | | | 10 | 2 | | | | | | | |
| 31 Gd | | | | | | 10 | 2 | 1 | | | | | | |
| 32 Ge | | | | | | 10 | 2 | 2 | | | | | | 4*p* full |
| 33 As | | | | | | 10 | 2 | 3 | | | | | | |
| 34 Se | | | | | | 10 | 2 | 4 | | | | | | |
| 35 Br | | | | | | 10 | 2 | 5 | | | | | | |
| 36 Kr | | | | | | 10 | 2 | 6 | | | | | | |
| 37 Rb | Krypton Core of 36 electrons | | | | | | | | | | 1 | | | |
| 38 Sr | | | | | | | | | | | 2 | | | 5*s* full |
| 39 Y | | | | | | | | | 1 | | 2 | | | |
| 40 Zr | | | | | | | | | 2 | | 2 | | | |
| 41 Cb | | | | | | | | | 4 | | 1 | | | |
| 42 Mo | | | | | | | | | 5 | | 1 | | | |
| 43 Tc | | | | | | | | | 6 | | 1 | | | |
| 44 Ru | | | | | | | | | 7 | | 1 | | | 4*d* full |
| 45 Rh | | | | | | | | | 8 | | 1 | | | |
| 46 Pd | | | | | | | | | 10 | | | | | |
| 47 Ag | | | | | | | | | 10 | | 1 | | | |
| 48 Cd | | | | | | | | | 10 | | 2 | | | |
| 49 In | | | | | | | | | 10 | | 2 | 1 | | |
| 50 Sn | | | | | | | | | 10 | | 2 | 2 | | |
| 51 Sb | | | | | | | | | 10 | | 2 | 3 | | 5*p* full |
| 52 Te | | | | | | | | | 10 | | 2 | 4 | | |
| 53 I | | | | | | | | | 10 | | 2 | 5 | | |
| 54 Xe | | | | | | | | | 10 | | 2 | 6 | | |

stable half filled 3*d* sublevel with five electrons (the full quota of a *d* sublevel is 10 electrons).

Similarly, copper (at. no. 29) has the configuration $1s^2$, $2s^2$, $2p^6$, $3s^2$ $3p^6$ $3d^{10}$, $4s^1$ rather than the expected $1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^6$ $3a^9$, $4s^1$. In this case one of 4*s* orbital electrons moves into a 3*d* orbital to make a stable fully filled 3*d* sublevel with 10 electrons

The ground state electronic configurations of the first 54 elements are given in Table 1-7 on page 30.

## 16. Atomic Number

Formerly, the atomic number of an element signified its serial number in an arrangement of elements according to their properties, *e.g.*, in the periodic table. It is now established that the *atomic number of an element is numerically equal to the number of unit positive charges on the nucleus of its atom*. Obviously, the atomic number is equal to the number of protons in the nucleus and therefore, also equal to the number of orbital electrons

**Atomic number is the fundamental property of the atom.** This fact was established experimentally by Moseley from a study of the X-ray spectra of various elements. Moseley used a discharge tube with high voltage and having an *anticathode* of the metal under study (or, an anticathode of platinum on which a compound of the element under study is applied). The strong electron bombardment on the anticathode excited the electrons of two inner shells of its atoms. These electrons on falling back to lower levels produced X-rays (Fig. 1-25). These X-rays were spread out into spectra on a photographic plate using a crystal of potassium ferrocyanide for diffration. The X-ray spectra showed certain prominent lines corresponding to rays of definite wavelengths which were characteristic of the element of the anticathode. The X-rays corresponding to these wavelengths are, therefore, called *characteristic X-rays* and they belong to different series—K, L, M series, etc.

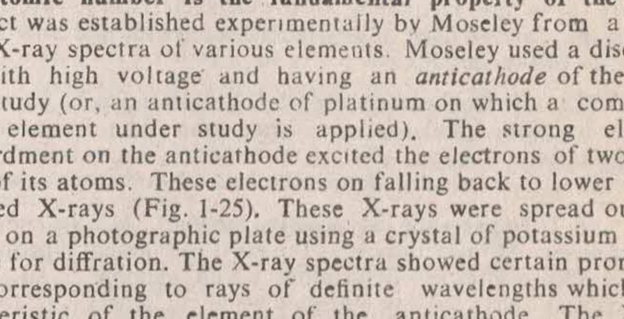

Fig. 1-25. Emission of X-rays when cathode rays strike the anticathode.

Moseley plotted a graph of the square root of the frequency ($\nu$) of the characteristic X-rays against the atomic number ($z$). He obtained a straight line for each series. When the same frequencies are plotted against atomic weights, no such relationship is observed. This shows that *atomic number and not atomic weight is the fundamental property of the atom.* The atoms of an element may have different weights (isotopes) but they have the same atomic number.

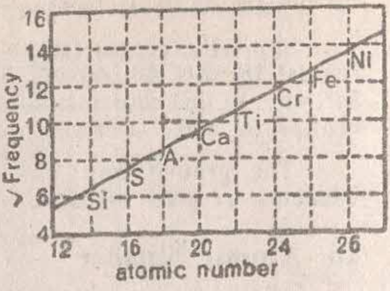

Fig. 1-26. Variation of X-rays frequency with atomic number.

**16-1. Determination of atomic number.** The experimental determination of atomic number is based on Moseley's law : *The square root of the characteristic frequency of X-rays from an element is a linear function of its atomic number.* Mathematically,

$$\nu=\sqrt{a}(z-b)$$

where $\nu$ is the frequency of the characteristic X-ray, $a$ and $b$ are constants for the lines of any particular series, and $z$ is the atomic number of the element.

The element whose atomic number is to be determined, is made an anticathode in an X-ray tube. The frequency of the characteristic X-rays, say of K series, is measured. The atomic number is then calculated with the help of the above relationship.

**16·2. Importance of atomic number.** (1) *In characterising an element.* Atomic number is the most fundamental property of an atom since it uniquely determines which element it is. Two elements may have the same atomic weights (*isobars*) or atoms of one and the same element may have different weights (*isotopes*), but the atomic number of an element is its unique property which characterizes only that element and no other.

(2) *As the basis of the periodic classification of elements.* Atomic number is the modern basis for periodic classification of elements. According to the modern periodic law, the properties of elements are a periodic function of their atomic numbers. Periodic tables based on atomic numbers are free from most of the defects found in tables based on atomic weights. The determination of the atomic number of an element undisputably settles its position in the periodic table.

(3) *In pin-pointing undiscovered elements.* Moseley's work conclusively shows that any gap between two nearest atomic numbers corresponds to an undiscovered element. This made the prediction and discovery of undiscovered elements possible. Thus, the atomic number of molybdenum (Mo) and ruthentium (Ru) were found to be 42 and 44 respectively. This showed the existence of an element of atomic number 43 which was subsequently discovered.

The study of atomic numbers shows that there are no more missing elements upto the element with atomic number 105.

(4) *In elucidating atomic composition.* The atomic number of an atom is numerically equal to the number of protons in its nucleus and the number of orbital electrons. Since atomic weight is practically equal to the total number of protons and neutrons, the numerical difference of atomic weight and atomic number gives the number of neutrons in the nucleus.

## Questions

1. (*a*) What are 'cathode rays' ? (*b*) What properties of cathode rays show that they are the streams of negatively charged tiny particles of matter ?

2. What evidence have we that electrons are among the constituents of all atoms ?

3. What are the positive rays ? How are they produced ? What are they composed of when produced from hydrogen ?

4. Give the names along with the relative mass and electrical charge of each one of the three fundamental particles of atoms.

5. How can atoms contain electrically charged particles and still be electrically neutral ?

6. What important conclusions are drawn from an experimental study of the scattering of fast moving alpha particles by a thin gold foil ?

7. Explain the terms 'atomic number' and 'mass number' of the atom. How can the knowledge of the atomic number and the mass number of an atom be used to determine the number of the three fundamental particles in it ?

8. What is the difference between a continuous spectrum and a discontinuous or line spectrum ? What type of spectrum is produced by an incandescent gas or vapour ?

9. Describe the main postulates of Bohr's atomic model ?

10. Name the five series of lines in the hydrogen spectrum stating the region in which each of them lies.

11. The hydrogen atom consists of only one electron. Yet, the spectrum of hydrogen shows a large number of lines. Explain.

12. State Heisenberg's uncertainty principle. How has it led to the concept of an atomic orbital ?

13. What do you understand by the terms 'energy level' and 'energy sublevels' ? How many energy sublevels exist in each one of the first four energy levels ? How are these sublevels designated ?

14. (a) Name the four quantum numbers which specify an electron within an atom.

(b) What is specified by each type of quantum number ?

15. Show on a labelled sketch the shapes and spatial distribution of all the orbitals of principal quantum number 2.

[**Hint.** These orbitals are $2s$, $2p_x$, $2p_y$, and $2p_z$.]

16. What are the limiting number of electrons in the shells K, L, M, and N ?

17. State the principle which limits the number of electrons in an atomic orbital to two.

18. Explain the maximum number of electrons in the fourth energy level in terms of energy sublevels, orbitals, and electron spins.

19. What is wrong with each of the following sets of quantum numbers.

(*a*) 2, 2, 0, $+\frac{1}{2}$
(*b*) 2, 0, 1, $+\frac{1}{2}$
(*c*) $-1$, 0, 0, $+\frac{1}{2}$.
(*d*) 2, 1, $+\frac{1}{2}$, $-\frac{1}{2}$

20. What is meant by the terms 'unpaired electrons' and paired electrons' ?

21. How many unpaired electrons are there in a silicon atom (at. no. =14) ?

22. How many unpaired electrons are there in a chlorine atom (at no. =17) ?

23. The electronic configuration of an element is represented as $1s^2$, $2s^2$, $2p^5$. What does this signify ?

24. The electronic configuration of an element of atomic number 11 can be written as $1s^2$, $2s^2$, $2p^6$, $3s^1$. In the same way write down the electronic configuration of an element of atomic number 35.

25. What is wrong with each of the following electron configurations:
(*a*) $1s^2$, $2s^4$ (*b*) $1s^2$, $2s^2\ 2p^6$, $3p^1$ (*c*) $1s^2$, $2s^2\ 2p^6$, $3s^2\ 3p^6\ 3d^{10}$ ?

26. Explain, with suitable examples, each of the following :

(*a*) Aufbau principle

(*b*) Hund's rule of maximum multiplicity.

27. (*a*) Explain the reason why the electron configuration of chromium atom is [Ar] $4s^1$, $3d^5$ and not [Ar] $4s^2$, $3d^4$ ?

(*b*) Explain the reason why copper atom has the electron configuration $1s^2$, $2s^2\ 2p^6$, $3s^2\ 3p^6\ 3d^{10}$, $4s^1$ and not $1s^2$, $2s^2\ 2p^6$, $3s^2$, $3p^6\ 3d^9$, $4s^2$.

28. State in brief the significance of atomic number.

29. Why do the atoms having the same atomic number but different atomic weights show exactly the same chemical properties ? What are such atoms called ?

## Key

5. An atom has equal number of protons (each carrying unit positive charge) and electrons (each carrying unit negative charge).

13. First energy level has one sublevel designated 1*s*, second energy level has two sublevels designated 2*s* and 2*p*, third has three sublevels designated 3*s*, 3*p*, and 3*d*, and the fourth one has four sublevels designated 4*s*, 4*p*, 4*d*, and 4*f*.

16. 2, 8, 18, and 32 respectively.

17. Pauli's exclusion principle (for statement see page 24).

18. The fourth energy level consists of sublevels 4*s*, 4*p*, 4*d*, and 4*f*. The 4*s* sublevel consists of a single orbital, the 4*p* sublevel consists of three orbitals, the 4*d* sublevel consists of five orbitals, and the 4*f* sublevel consists of seven orbitals. So, the total number of orbitals in various sublevels is $1+3+5+7=16$. Each orbital can be occupied by a maximum of two electrons of opposite spins. Hence, the maximum number of electrons in the fourth energy level is $16\times2=32$

19. (*a*) When $n=2$, $l$ can only be 0 or 1, not 2.
(*b*) When $l=0$, $m$ can only be 0, not 1.
(*c*) $n$ can only be positive, integral values, not negative.
(*d*) $m$ can only be integral values between $+l$ and $-l$; therefore it cannot be $+\frac{1}{2}$.

20. A single electron in an orbital is an unpaired electron; two electrons in an orbital spin in opposite directions (spin quantum number $= +\frac{1}{2}$ and $-\frac{1}{2}$) and are said to be paired.

21. Using the aufbau order, the electron configuration for silicon is $1s^2$, $2s^2\, 2p^6$, $3s^2\, 3p^2$. Since all orbitals through the $3s$ sublevel are filled, we have to consider only the $3p$ orbitals accomodating two electrons. Since, there are three $p$ orbitals, both electron will occupy separate orbitals. Hence, there are two unpaired orbitals.

22. The electron configuration of chlorine is $1s^2$, $2s^2\, 2p^6$, $3s^2\, 3p^5$. In this case five electrons are accomodated in the three $3p$ orbitals. Hence, two of these orbitals will have two orbitals each an one will have only one electron. Hence, there is one unpaired electron.

25. (*a*) An $s$ sublevel can have a maximum of two electrons; so, it cannot be $2s^4$.

(*b*) The electrons entering third energy level will first occupy $s$ sublevel and not the $p$ sublevel.

(*c*) According to aufbau principle, the $4s$ sublevel fills after $3p$, not the $3d$ sublevel.

26. (*a*) Because a half filled $3d$ sublevel is more stable. (*b*) Because a fully filled $3d$ sublevel is more stable.

□ □

## 2

# The Periodic Table

The periodic relationship of chemical elements, which is reflected in similar elements recurring periodically when properly arranged, is the broadest and the most useful single concept in chemistry. This relationship is not an accident, it is a direct consequence of the structures of atoms. The chemical and physical properties of elements are determined by the number and arrangements of the orbital electrons, *i.e.*, by their electronic structures. *The elements with similar electronic configurations, therefore, exhibit similar properties,*

The tabular arrangement of elements which brings out their periodicity is called a *periodic table.* The first periodic tables were constructed independently by Mendeleev in Russia and Lothar Meyer in Germany in 1869. Many forms of the periodic table have been constructed since then. Of these, the so called *long form periodic table* is not only the simplest but also very useful for a general study of elements. The most important use of any periodic table lies in its ability to accommodate and summarize a vast body of facts pertaining to chemical elements and their compounds.

## 1. Historical Background*

**(1) Prout's hypothesis.** The search for regularities among the elements began early in the 19th century when only some 50 elements were known. The first significant attempt was made as early as 1815 when Prout ventured a hypothesis that all elements were, in some way, multiples of the element hydrogen (*Prout's unitary hypothesis*). In a way, this view is correct if we consider how atoms are built up from the same elementary particles. However, the evidence at that time was not enough to justify the hypothesis, and so it was rejected.

**(2) Dobereiner's triads.** In 1829 Dobereiner identified certain groups of three elements having similar properties which he called triads. Some examples of triads are : Li, Na, K; Cl, Br, I; and Ca, Sr, Ba. The similarity in the 'triad elements' appeared to be related in some way to atomic weights since, when arranged according to increasing atomic weight, the atomic weight of the middle element was always midway between the atomic weights of the other two. Sodium's atomic weight (23), for example, is midway between that of lithium (7) and potassium (39). and bromine's atomic weight (80) is about midway between chlorine's 35·5 and iodine's 127. However, this relationship was simply accidental.

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*Questions will not be set on the historical development of the Periodic Table.

In 1851 Dumas showed that in some cases more than three elements showed close resemblances in their chemical properties *e.g.*, N, P, As, Sb, Bi.

**(3) Newland's law of octaves.** In 1865 newlands showed that when elements were arranged in the order of their atomic weights, beginning with the lightest one (after omitting hydrogen), "*the eighth element, starting from a given one, is a kind of repetition of the first, like the eighth note in an actave of music.*" Thus, the idea of periodicity among elements was born. However, Newland's classification (Table 2-1) broke down after the first 16 elements for he did not leave gaps for undiscovered elements.

**Table 2-1** *Newland's classification of elements*

| | | | | | | |
|---|---|---|---|---|---|---|
| Li | Be | B | C | N | O | F |
| Na | Mg | Al | Si | P | S | Cl |
| K | Ca | | | | | |

**(4) Lothar Meyer's curve.** In 1869 Lothar Meyer plotted the atomic weights of elements against their atomic volumes (the ratio between atomic weight in grams and the density in the solid state). In the curve, similar elements occupied similar positions, thus forming distinct groups. For example, the alkali metals (Li, Na, K, Rb, Cs) are at the peaks and the halogens (F, Cl, Br, I) midway on the ascending portions of the curve.

**(5) Mendeleev's periodic law.** In 1969, Mendeleev classified elements on the basis of the periodic law which he stated as follows : "*the properties of elements are a periodic function of their atomic weights*". This means that when elements are arranged in the order of increasing atomic weight similar elements will be repeated at definite intervals or periods.

**1-1. Mendeleev's periodic table.** Mendeleev, in 1969, arranged the elements (only some 60 were then known) in their sequence of increasing atomic weights in a manner that similar elements came one below another in vertical columns. The resulting tabular arrangement of elements was called the ***periodic table of elements*** (Table 3-2). When the order of the elements appeared to be broken, gaps were left with the idea that these places belonged to the elements yet undiscovered. For example, the element arsenic (As) was allocated place two gaps after zinc (Zn). The reason was that arsenic resembles phosphorus (P) two places away from zinc and not aluminium next to zinc or silicon one place away from zinc. He named the missing elements ***ekaaluminium*** ("one beyond aluminium") and ***ekasilicon*** ("one beyond silicon") respectively. Confident of the periodic relationship among elements, Mendeleev ventured to predict the properties of these elements by comparison with those of the neighbouring elements. When these elements were isolated and their properties noted, his predictions proved to be amazingly correct.

The soundness of Mendeleev's periodic table was further proved when a whole family of new elements, the noble gases, was accomodated by simply adding a vertical column to the table at the extreme right.

One form of Mendeleev's periodic table, improved in several respects and brought up to date by the inclusion of inert gases and other elements not known earlier is shown on page 39. It consists of seven horizontal rows of elements called *periods*, numbered in Arabic numerals form 1 to 7, and nine vertical columns, called *groups*. The groups are labelled consecutively in Roman numerals from I to VIII, the ninth group being labelled 0 (zero). The zero group was not there in Mendeleev's original table.

The first period is occupied by only two elements, hydrogen and helium. The second and third periods contain 8 elements each (Li to Ne; Na to Ar) and are called *short periods*. The fourth and fifth periods are *long periods* of elements each (K to Kr; Rb to Xe). The sixth is a *very long period* of 32 elements (Cs to Rn). This period has been compressed by placing 15 elements in a single space beyond barium. These elements called *rare earth metals* or *lanthanides* (57-71), are much alike chemically. The seventh is an *incomplete period*, consisting at present of 16 radioactive elements. The eleven elements beyond uranium in this period are called *transuranium elements*. Except francium (87) and radium (88), the elements of this period (89-103) constitute the *actinide series*. All the elements of this series have not yet been discovered.

The long periods have been doubled back into two series as a consequence of which each one of the groups from I to VIII stands subdivided into two sub-groups, A and B.

The periods contain series of elements in which the chemical properties change *qualitatively* in discrete steps. For example, in the third period, the first three metals (Na, Mg, and Al) are metals appearing in order of decreasing activity with a reagent such as water. The next four elements (Si, P, S, and Cl) are nonmetals, and they are seen in order of increasing activity with a reagent such as sodium or magnesium. The last element, argon (Ar) is chemically inactive, and as we shall see later, is represents the logical coclusion of the period. The properties of elements in a group, on the other hand, change only *quantitatively* from top downward. For example, all the elements in group IA react readily with water, acids, and the halogens, but the reactions become progressively more vigorous from lithium to francium.

**Table 2-2** *Mendeleev's periodic table (modified form)*

| Group → | I | | II | | III | | IV | | V | | VI | | VII | | VIII | Zero |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Oxide : Hydride ; | $R_2O$ RH | | RO $RH_2$ | | $R_2O_2$ $RH_3$ | | $RO_2$ $RH_4$ | | $R_2O_2$ $RH_3$ | | $RO_3$ $RH_2$ | | $R_2O_7$ RH | | $RO_4$ Transition Triads | Inert gases |
| Period ↓ | A | B | A | B | A | B | A | B | A | B | A | B | A | B | | |
| 1 | H 1 (At. No.)<br>1·008 (At. Wt) | | | | | | | | | | | | | | | He 2<br>4·0026 |
| 2 | Li 3<br>6·939 | | Be 4<br>9·012 | | B 5<br>10·81 | | C 6<br>12·011 | | N 7<br>14·007 | | O 8<br>15 999 | | F 9<br>18·998 | | | Ne 10<br>20·183 |
| 3 | Na 11<br>22 99 | | Mg 12<br>24 31 | | Al 13<br>26·98 | | Si 14<br>28·09 | | P 15<br>30·74 | | S 16<br>32·06 | | Cl 17<br>35·453 | | | Ar 18<br>39·948 |
| 1st series 4 | K 19<br>39 102 | | Ca 20<br>40·08 | | | Sc 81<br>44·96 | | Ti 22<br>47·90 | | V 23<br>50·94 | | Cr 24<br>32·00 | | Mn 25<br>54 94 | Fe 26 Co 27 Ni 28<br>55·85 58 93 58·71 | |
| 2nd series | | Cu 29<br>63·54 | | Zn 30<br>65·37 | Ga 31<br>69·72 | | Ge 32<br>72·59 | | As 33<br>74·92 | | Se 34<br>78·96 | | Br 35<br>79·909 | | | Kr 34<br>83 80 |
| 1st series 5 | Rb 37<br>85·47 | | Sr 38<br>87·62 | | | Y 39<br>88 90 | | Zr 40<br>91·22 | | Nb 41<br>92·91 | | Mo 42<br>95·94 | | Tc 43<br>99 | Ru 44 Rh 45 Pd 46<br>101·07 102·90 106·4 | |
| 2nd series | | Ag 47<br>107·87 | | Cd 58<br>112·40 | In 49<br>114·82 | | Sn 50<br>118·69 | | Sb 51<br>121·75 | | Te 52<br>127·60 | | 1·53<br>126·90 | | | Xe 54<br>131·30 |
| 1st series 6 | Cs 55<br>132·90 | | Ba 56<br>137·34 | | | Rare Earths<br>57—71 | | Hf 72<br>178·49 | | Ta 73<br>180·95 | | W 74<br>183 85 | | Re 75<br>186·2 | Os 76 Ir 77 Pt 78<br>190·2 192·2 195·09 | |
| 2nd series | | Au 79<br>196 97 | | Hg 80<br>200·59 | Ti 81<br>204·37 | | Pb 82<br>207·19 | | Bi 83<br>208·98 | | Po 84<br>(210) | | At 84<br>(210) | | | Rn 86<br>(222) |
| 7 | Fr 87<br>(223) | | Ra 88<br>(226) | | | Actinide Elements<br>89—103 | | | | | | | | | | |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Lanthanide series** (*Rare earth series*) | La 57<br>138·91 | Ce 58<br>140·12 | Pr 59<br>140·91 | Nd 60<br>144·24 | Pm 61<br>(145) | Sm 62<br>150·35 | Eu 63<br>151·96 | Gd 64<br>157·25 | Tb 65<br>158·92 | Dy 66<br>162·50 | Ho 67<br>164·93 | Er 68<br>167·26 | Tm 69<br>168·93 | Yb 70<br>173·04 | Lu 71<br>174 97 |
| **Actinide series** *Radioactive elements* | Ac 89<br>(227) | Th 90<br>232·04 | Pa 91<br>(231) | U 94<br>238·03 | Np 93<br>(237) | Pu 94<br>(244) | Am 95<br>(243) | Cm 96<br>(245) | Bk 97<br>(247) | Cf 98<br>(249) | Es 99<br>(254) | Fm 100<br>(252) | Md 101<br>(256) | No 102<br>(254) | Lw 103<br>(257) |

## 2. Modern Periodic Law

The physical and chemical properties of elements are determined by the magnitude of nuclear charge and the number of orbital electrons in their atoms. Both of these quantities are represented by *atomic number*. Hence, the periodicity of elements is a function of atomic number, rather than of atomic weight.*

Consequently, the periodic law is now stated as follows :

*When the elements are arranged in order of their increasing atomic numbers, their physical and chemical properties vary periodically.*

## 3. The Long Form Periodic Table

The *long form periodic table*, so called because of its general shape, is the most popular modification of the Mendeleev's periodic table. It has atomic number as the basis for setting up the sequence of elements. The most significant feature of the long form periodic table is that it has each period spread out in a single row. This arrangement avoids the confusion arising from the staggering of the long periods and the subdivision of the elements in the same vertical column into two subgroups as in the Mendeleev's table. The long form periodic table is given on page 41.

**3-1. Structure of long form periodic table**. The long form periodic table is divided into seven horizontal rows of elements arranged in the order of increasing atomic number, and eighteen vertical columns. The horizontal rows, called ***periods***, are numbered 1 to 7, inclusive from left to right. The vertical columns, called ***groups***, are consecutively labelled IA, IIA, IIIB, IVB, VB, VIB, VIIB, VIII, IB, IIB, IIIA, IVA, VA, VIA, VIIA and 0 (the B groups contain the transition elements). Group VIII is subdivided in three columns, making a total of eighteen vertical column. The division of the elements into periods and groups is directly related to the ground state structures of their atoms.

**3-2. Periods**. A period is a series of elements the atoms of which have the same number of electron shells. *Each period begins with an element that has one electron in a new main energy level.* Thus, the serial number of a period is the same as the principal quantum number *n* of the outer shell. The successive elements in the period have their energy sub-levels (or, subshells) filled according to the aufbau principle (Chapter 1, page 27). The number of elements in each period is determined by the sequence in which the various energy sub-levels are filled as shown in Table 2-4, page 42.

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*In general, the atomic weight varies in the same order as the atomic number. Hence, the periodicity of elements in Mendeleev's table, too, is related to the sequences of atomic number.

Table 2-3

*The long form Periodic Table*

| | *s* block | | *d* block | | | | | | | | | | *p* block | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Group ↓<br>Period → | Al | A | IIIB | IVB | VB | VIB | VIIB | VIII | | | IB | IIB | IIIA | IVA | VA | VIA | VIIA | 0 |
| 1 ; n = 1 | 1<br>H | | | | | | | | | | | | | | | | 1<br>H | 2<br>He |
| 2 ; n = 2 | 3<br>Li | 4<br>Be | | | | | | | | | | | 5<br>B | 6<br>C | 7<br>N | 8<br>O | 9<br>F | 10<br>Ne |
| 3 ; n = 3 | 11<br>Na | 12<br>Mg | | | | | | | | | | | 13<br>Al | 14<br>Si | 15<br>P | 16<br>S | 17<br>Cl | 18<br>Ar |
| 4 ; n = 4 | 19<br>K | 20<br>Ca | 21<br>Sc | 22<br>Ti | 23<br>V | 24<br>Cr | 25<br>Mn | 26<br>Fe | 27<br>Co | 28<br>Ni | 29<br>Cu | 30<br>Zn | 31<br>Ga | 32<br>Ge | 33<br>As | 34<br>Se | 35<br>Br | 36<br>Kr |
| 5 ; n = 5 | 37<br>Rb | 38<br>Sr | 39<br>Y | 40<br>Zr | 41<br>Nb | 42<br>Mo | 43<br>Tc | 44<br>Ru | 45<br>Rh | 46<br>Pd | 47<br>Ag | 48<br>Cd | 49<br>In | 50<br>Sn | 51<br>Sb | 52<br>Te | 53<br>I | 54<br>Xe |
| 6 ; n = 6 | 55<br>Cs | 56<br>Ba | 57<br>La | 72<br>Hf | 73<br>Ta | 74<br>W | 75<br>Re | 76<br>Os | 77<br>Ir | 78<br>Pt | 79<br>Au | 80<br>Hg | 81<br>Ti | 82<br>Pb | 83<br>Bi | 84<br>Po | 85<br>At | 86<br>Rn |
| 7 ; n = 7 | 87<br>Fr | 88<br>Ra | 89<br>Ac | 104<br>Ku | 105<br>Ha | | | | | | | | | | | | | |

*f* block

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lanthanides | 58<br>Ce | 59<br>Pr | 60<br>Nd | 61<br>Pm | 62<br>Sm | 63<br>Eu | 64<br>Gd | 65<br>Tb | 66<br>Dv | 67<br>Ho | 68<br>Er | 69<br>Tm | 70<br>Yb | 71<br>Lu | |
| Actinides | 90<br>Th | 91<br>Pa | 92<br>U | 93<br>Np | 94<br>Pu | 95<br>Am | 96<br>Cm | 97<br>Bk | 98<br>Cf | 99<br>Es | 100<br>Fm | 101<br>Md | 102<br>No | 103<br>Lr | |

**Table 2.4** *Number of elements in the periods*

| Period | Filling up of energy levels | | | | No. of elements |
|---|---|---|---|---|---|
| 1st period | 1s | | | | 2 |
| 2nd period | 2s | | | 2p | 2+6=8 |
| 3rd period | 3s | | | 3p | 2+6=8 |
| 4th period | 4s | | 3d | 4p | 2+10+6=18 |
| 5th period | 5s | | 4d | 5p | 2+10+6=18 |
| 6th period | 7s | 4f | 5d | 6p | 2+14+10+6=32 |

The 7th period can also have 32 elements with the filling up of $7s$, $5f$, $6d$, and $7p$ energy levels, but it is still incomplete with only 19 elements with atomic numbers up to 107. In each period (except the first one), the first element is an alkali metal with a $1s$ electron in the outer level and the last element is an inert gas with completed $s$ and $p$ sublevels in the outer shell ($s^2p^6$ ending).

*First period* has two elements — hydrogen, $1s^1$, and helium, $1s^2$, corresponding to the filling of the first energy level ($n=1$).

*Second period* begins with the third element, lithium, which has an electron in the $s$ sublevel of the second main energy level ($n=2$). The period is completed at neon which has $s$ and $p$ sublevels completely filled and, thus, has the maximum possible number of electrons in the second shell.

*Third period* begins with the filling in of the energy level, $n=3$, consisting of $3s$, $3p$, and $3d$ sub-shells. The first element is sodium, $_{11}$Na, with one electron in the $3s$ sublevel. In the last element argon, $_{18}$Ar, the $3s$ and $3p$ sub-levels are complete, but the orbitals of the $3d$ sub-shell remain empty. This is because the next electron goes to the energywise more favourable $4s$ level and not to the $3d$ level.

*Fourth period* begins with potassium, $_{19}$K, which has one electron in the $4s$ sublevel ($n=4$). The next element calcium, $_{20}$Ca, has the $4s$ level completely filled with 2 electrons. In both of these elements, the $3d$ level is wholly vacant

| | | | | |
|---|---|---|---|---|
| $_{19}$K | $1s^2$ | $2s^22p^6$ | $3s^23p^63d^0$ | $4s^1$ |
| $_{20}$Ca | $1s^2$ | $2s^22p^6$ | $3s^23p^63d^0$ | $4s^2$ |

In the successive elements, the $3d$ level is progressively filled and is completed at zinc with 10 electrons.

| | | | | |
|---|---|---|---|---|
| $_{21}Sc$ | $1s^2$ | $2s^2 2p^6$ | $3s^2 3p^6 3d^1$ | $4s^2$ |
| $_{22}Ti$ | $1s^2$ | $2s^2 2p^6$ | $3s^2 3p^6 3d^2$ | $4s^2$ |
| . . . . | | | | |
| . . . . | | | | |
| $_{25}Mn$ | $1s^2$ | $2s^2 2p^6$ | $3s^2 3p^6 3d^5$ | $4s^2$ |
| $_{26}Fe$ | $1s^2$ | $2s^2 2p^6$ | $3s^2 3p^6 3d^6$ | $4s^2$ |
| . . . . . | | | | |
| . . . . . . | | | | |
| . . . . . | | | | |
| $_{30}Zn$ | $1s^2$ | $2s^2 2p^6$ | $3s^2 3p^6 3d^{10}$ | $4s^2$ |

After the $3p$ level has been completed, the $p$ sub-level of the outer shell, *i.e.*, the $4p$ sub-level begins to be filled in the next six elements (Ga—Kr). Thus, the fourth period corresponds to the filling of the $4s$, $3d$, and $4p$ sub-levels. The introduction of ten $3d$ electrons expands the fourth period from eight to eighteen elements.

***Fifth period*** follows the same pattern as the fourth period, and corresponds to the filling of the $5s$, $4d$, and $5p$ sublevels. The outer level ($n=5$) is filled in the $s$ sublevel in the first two elements, $_{37}Rb$ and $_{38}Sr$, and in the $p$ sub-level in the last six elements ($_{49}In$—$_{54}Xe$); in the intervening ten elements ($_{39}Y$—$_{48}Cd$) the $d$ sublevel of the next inner shell (*i.e.*, the $4d$ subshell) is filled. Just as the third period concluded with the outer level incomplete in the $d$ subshell (*i.e.*, $3d$ sub-shell) the sixth period is completed with the $f$ subshell of the outer level (*i.e.*, $4f$ sub-shell) wholly vacant.

***Sixth period*** begins with caesium, $_{55}Cs$, which has one electron in the $s$ sub-level of the main energy level, $n=6$. The elements in the period correspond to the filling of the $6s$, $4f$, $5d$, and $6p$ sublevels, the fourteen elements ($_{58}Ce$—$_{71}Lu$) corresponding to the addition of electrons in the $4f$ sub-level are placed alongwith lanthanum, $_{57}La$*, in a separate row at the bottom of the table. All these elements have the same number of electrons in the outer shell, and hence in the main table they have all been placed together in a single box. These elements are called the ***lanthanides***. These fourteen elements expand the sixth period to a total of thirty two elements.

***Seventh period*** is analogous to the sixth period. It begins with francium $_{87}Fr$, having one electron in the $s$ sublevel of the outer shell ($n=7$). It is followed by radium, $_{88}Ra$, in which the $7s$ sub-level is completed. The next element actinium, $_{89}Ac$, has the new electron in the $6d$ sub-level rather than in the $5f$ level (compare with $_{57}La$). The next fourteen elements ($_{90}Th$—$_{103}Lr$) correspond to the filling of the $5f$ sub-level. These are also placed in a separate row, along with actinium, at the bottom of the table, and are called the ***actinides***. The elements following the last actinide, $_{103}Lr$, have the new electrons in the $6d$ sub-level. The seventh period is incomplete, and can contain a total of 32 elements. Additions are being made by synthetic elements and the last reported synthetic element has the atomic number 107.

---

*$_{57}La$ has one electron in the $5d$ level rather than in the $4f$ level. Its configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 5d^1\ 6s^2$,

**3-3. Groups.** The vertical columns of elements in the periodic table are called groups. Each group of elements has in common a particular number of *valence electrons*—the electrons in the outermost energy levels. Since the chemical behaviour of the elements is primarily affected by the valency electrons, the elements of each group exhibit strikingly similar properties. Thus, the elements of group IA all have the outer level electronic configuration, $ns^1$, and those of IIA, $ns^2$. The elements in groups IIIA to 0 have the outer level or *valence shell* electron configuration varying from $ns^2np^1$ to $ns^2 np^6$. The outer two shells configuration of the ten groups between the groups IIA and IIIA is $(n-1)\ d^{1-10}\ ns^{1-2}$. In group IIIB, there are two groups of fourteen elements each, one with lanthanum, and the other with actinium is the first element. The outer three shells configurations of these groups of elements, called the lanthanides and the actinides respectively, is $(n-2)\ f^{1-14}\ (n-1)\ d^{0-2}\ ns^2$.

Group VIII of the periodic table is a special case inasmuch as three vertical columns bear this label. The elements of this group, nine in all, have so many valence electrons that the total number is not much significant, and chemical behaviour is determined largely by other factors. As a result, their properties do not significantly change across the period, and all of them have been put in a single group.

## 4. Periodicity in Properties

The properties of elements are determined by their electronic configurations, particularly the electrons in the outer levels. These electrons, called valence electrons, take part in all chemical reactions. The loss, gain, or sharing of these electrons in chemical reactions is governed by two interrelated factors: (1) the magnitude of nuclear charge, which is equal to the atomic number, and (2) the distance of the valence shell (outer level) from the nucleus, *i.e.*, the atomic radius. The properties of elements, therefore vary periodically with atomic number across the periods and down the groups. They change in discrete steps in the horizontal direction, *i.e.*, across the periods as the number of valence electrons successively increases, and are repeated at definite intervals vertically downward, *i.e.*, in groups as similar electronic structures are repeated. The periodicity in properties is, thus, a reflection of the periodicity of electron structures. This is illustrated for the elements of the second and third periods in Table 2-5.

**Table 2-5.** *Electronic configurations of elements of periods 2 and 3*

| Group ↓ | IA | IIA | IIIA | IVA | VA | VIA | VIIA | O |
|---|---|---|---|---|---|---|---|---|
| Period 2→ | Li | Be | B | C | N | O | F | Ne |
| Electronic Configuration | 2,1 | 2,2 | 2,3 | 2,4 | 2,5 | 2,6 | 2,7 | 2,8 |
| Period 3→ | Na | Mg | Al | Si | P | S | Cl | Ar |
| Electronic Configuration | 2,8,1 | 2,8,2 | 2,8,3 | 2,8,4 | 2,8,5 | 2,8,6 | 2,8,7 | 2,8,8 |

In the long periods, elements with similar electronic configurations recur after 18, 18, and 32 elements. Thus, elements with similar electronic configurations fall below one another in vertical groups. For example, all the alkali metals of group IA have a single valence electron. They are, therefore, monovalent, strongly electropositive elements. The halogens of Group VIIA have seven valency electrons. They are, therefore, monovalent, strongly electronegative elements. Compare the outer shells in other vertical columns in the same way.

| ALKALI METALS | | | HALOGENS | | |
|---|---|---|---|---|---|
| Lithium, | Li | 2, 1 | Fluorine, | F | 2, 7 |
| Sodium, | Na | 2, 1 | Chlorine, | Cl | 2, 8, 7 |
| Potassium, | K | 2, 8, 8, 1 | Bromine, | Br | 2, 8, 18, 7 |
| Rubidium, | Rb | 2, 8, 18, 1 | Iodine, | I | 2, 8, 18, 18, 7 |
| Cesium, | Cs | 2, 8, 18, 18, 8, 1 | Astatine, | At | 2, 8, 18, 32, 18, 7 |
| Francium, | Fr | 2, 8, 18, 32, 18, 8, 1 | | | |
| (Number of valency electrons = 1) | | | (Number of valency electrons = 7) | | |

In the following sections, we shell study the periodicity in atomic radii and atomic volume, ionic radii, ionization energy, and electron affinity. Since, the chemical behaviour of elements and their non-metallic or metallic character is determined by these properties, the knowledge of the trends of their variation in the periodic system is of great value in predicting the properties of an element from its position in the periodic table.

## 5. Atomic Radii

The boundary of an atom's electronic field is not sharply defined, but is somewhat fuzzy and indefinite. Hence, it is difficult to define the sizes of atoms and even more difficult to measure them experimentally. However, the approximate radii of atoms can be estimated from measured distances between the nuclei of neighbouring atoms, either in molecules or in solids. Two generalizations can be made regarding the variations in atomic radii in the periodic table.

1. **The atomic radii decrease from left to right within a period.** The reason is that while the number of occupied shells remains the same, the nuclear charge of each succeeding element across a period is higher by one unit. Hence, there is greater attraction of the increasing nuclear charge for electrons entering the same shell, which is pulled increasingly inward towards the nucleus. However, the atomic radius of the inert gas at the end of the period is greater than that of the preceding element (a halogen). This is due to the structural stability of an outer shell consisting of eight electrons. The variation of atomic radii of elements in the third period is summarized in Table 3-7.

**Table 3-7.** *Atomic radii af elements in 3rd period*

| | Na | Mg | Al | Si | P | S | Cl | Ar |
|---|---|---|---|---|---|---|---|---|
| Nuclear charge | +11 | +12 | +13 | +14 | +15 | +16 | +17 | +18 |
| Electronic stucture | 2,8,1 | 2,8,2 | 2,8,3 | 2,8,4 | 2,8,5 | 2,8,6 | 2,8,7 | 2,8,8 |
| Atomic radius, A° | 1.86 | 1.60 | 1.48 | 1.17 | 1.10 | 1.04 | 0.99 | 1.54 |

2. **The atomic radii increase with atomic number in a particular group.** This is because each element in a group has one more electron shell than the element above it. The effect of increased nuclear charge in decreasing the atomic radii is insignificant as compared to the increase consequent upon the addition of a new electron shell. The variation of atomic radii in the elements of group IA is presented in Table 2-6.

**Table 2-6.** *Atomic radii of elements of group IA*

| Element (Symbol) | Nuclear charge (=atomic number) | Electronic structure | Number of electron shells | Atomic radius A° |
|---|---|---|---|---|
| Li | +3 | 2,1 | 2 | 1.52 |
| Na | +11 | 2,8,1 | 3 | 1.86 |
| K | +19 | 2,8,8,1 | 4 | 2.31 |
| Rb | +37 | 2,8,18,8,1 | 5 | 2.44 |
| Cc | +55 | 2,8,18,18,8,1 | 6 | 2.62 |

The atomic sizes of first twenty elements, excluding the inert gases He, Ne, and Ar, are shown diagrammatically in Fig. 2-1.

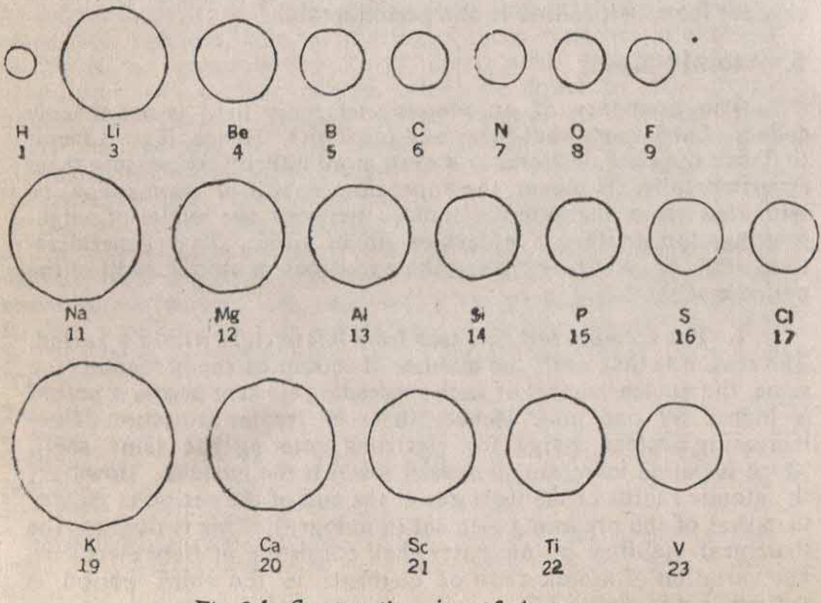

Fig. 2-1. Comparative sizes of atoms.

## 6. Atomic Volume

Formerly, the atomic radii of elements were estimated from their gram atomic volumes, defined as the volumes of one gram-atom of each element. The gram atomic volumes are calculated by dividing the atomic weights (in grams) by the densities of elemental solids, both values being obtained experimentally. That is, V=M/D, where V is gram atomic volume, M, the atomic weight in grams, and D the density in grams per cm$^3$. Thus, for gold the gram atomic volume,

$$V g\text{-atom} = \frac{197.2 g/g\text{-atom}}{19.3 g/cm^3}$$
$$= 10.22 \text{ cm}^3/g\text{-atom}$$

Since, one gram atom of an element contains one Avogadro number of atoms ($6{\cdot}02 \times 10^{23}$), the volume of a single atom can be worked out, and from it the atomic radius assuming that the atom is spherical. The trend in the variation in the atomic volume with the increasing atomic number is similar to that of atomic radii. Fig. 2-2 shows the variation in atomic volume among elements against the atomic number. It is seen that the atomic volumes of Li, Na, K, Rb, and Cs increase in the same order as do their atomic radii.

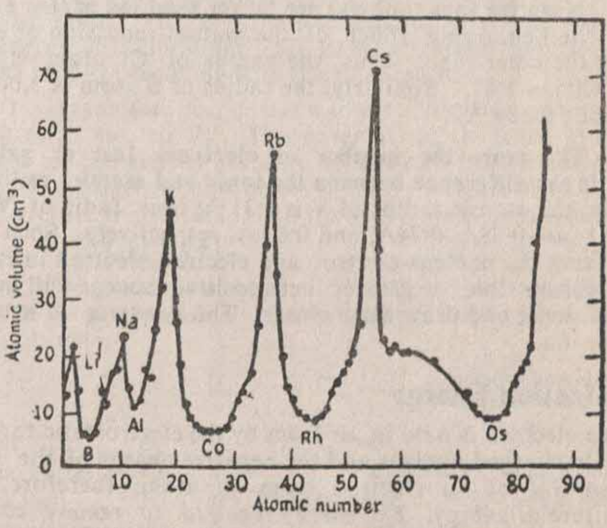

Fig. 2-2. Atomic volumes of the elements.

The comparison of atomic volumes of the elements in a period is not very reliable since atoms of different elements often pack in different arrangements. However, in a group all elements have similar packing pattern and atomic volumes do reflect the relative sizes of atoms.

## 7. Ionic Radii

When atoms lose electrons, positive ions or cations are formed which carry as many units of positive charge as the number of electrons lost ($A \rightarrow A^{n+} + ne^-$). When atoms gain electrons, negative ions or anions are formed which bear as many units of negative charge as the number of electrons gained ($A + ne^- \rightarrow A^{n-}$). The radii of various ions are derived from distances between ions in crystals. For example, the sizes of sodium ion ($Na^+$) and chloride ion ($Cl^-$) may be derived in part by measuring the internuclear distances in sodium chloride. This distance, as determined by experiment is 2·75 Å. It is equal to the sum of the corresponding ionic radii. However difficulty arises in estimating the share of each ion in this distance. This difficulty has been solved by measuring many ionic crystals in which these ions are present.

Following generalizations can be made about ionic radii.

1. **Positive ions (cations) are always smaller than the paren, atom.** This is because positive ions are formed by loss of electronst often a complete electron shell. For example, $_{11}Na$ (2,8,1) has three electron shells; $Na^+$ ion (2,8) formed by the loss of the lone electron in the outer shell has two shells. As such, the radius of the $Na^+$ ion is 0·95 Å against 1·86 Å of Na atom. Similarly, the radius of $Mg^{2+}$ ion (2,8) is 0·65 Å; of Mg atom (2,8,2) is 1·60 Å.

2. **Negative ions (anions) are larger than the parent atom** due to the shell-enlarging effect of the mutual repulsion of electrons entering the outer shell. Thus, the radius of Cl atom is 0·99 A; that of $Cl^-$ion 1·81. Similarly, the radius of S atom is 1.04 Å, that of $S^{2-}$ ion is 1·84 Å.

3. **The more the number of electrons lost or gained, the greater is the difference between the ionic and atomic radii.** As an example, the atomic radius of V is 1·31 Å; ionic radii of $V^{2+}$, $V^{3+}$, and $V^{4+}$ are 0·88Å. 0·74Å, and 0·60 Å, respectively. Such changes follow from the nucleus-electron and electron-electron interactions. In a positive ion, a greater net positive charge will act on the electron shells and draw them closer. The converse is true for a negative ion.

## 8. Ionization Energy

An electron is held in an atom by the electrostatic force of the positively charged nucleus and the negative charge of the electron. The removal of an electron from an atom, therefore, requires expenditure of energy. *The energy required to remove completely the most loosely bound (i.e., the highest-energy) electron from an atom in the gaseous state is called the ionization energy or ionization potential.* That is. it represents the energy absorbed in the ionization reaction,

$$M(g) + \text{energy} \rightarrow M^+(g) + e^-$$

The ionization energies are expressed in electron volts per atom (eV/atom) or kilojules per Avogadro number of atoms (kJ $mol^{-1}$). One ev/atom is equivalent to 23 kilocal. or 96 3 kJ $mol^{-1}$.

The energy involved in removing the first electron from the atom is more appropriately called the *first ionization energy*. The energy involved in removing the second electron is the *second ionization energy*. Third, fourth, and successive ionization energies may be defined in a similar fashion.

Following generalizations on the variation in ionization energy may be drawn :

1. In general, **the ionization energy increases across a period on the periodic table** The two factors responsible for this trend are the decreasing size of the atom (with increased electrostatic attraction) and higher nuclear charge in each succeeding element. However, the increase in ionization energy is regular. Two points of break appear in the variation in the ionization energies of the elements of the second period (Table 2-7).

(*i*) Boron (at. no 5) has a lower ionization energy than beryllium (at. no. 4), contrary to the general trend. This is because the electron removed in the ionization of boron is a *p* electron whereas an *s* electron is removed in the ionization of beryllium On the average an *s* electron approaches the nucleus more closely than a *p* electron of the same main energy level, and, therefore, the ionization energy of a *p* electron is less than that of an *s* electron in the same shell. This explanation also holds for the lower ionization energy of aluminium (578 kJ $mol^{-1}$) than that of magnesium (732 kJ $mol^{-1}$) preceding it in the third period.

(*ii*) Oxygen (at. no. 8) has a lower ionization energy than that of nitrogen (at. no. 7). The reversal of the trend in this case is related to the greater stability of the half-filled orbitals in a sub-shell. In nitrogen, the *p* sub-level of the valence shell is half-filled and therefore more stable than the *p* sub-level in oxygen.

$$\boxed{\uparrow}\ \boxed{\uparrow}\ \boxed{\uparrow} \qquad\qquad \boxed{\uparrow\downarrow}\ \boxed{\uparrow}\ \boxed{\uparrow}$$

**2*p* sub-shell in nitrogen** **2*p* sub-shell in oxygen**

As such a *p* electron is removed more readily from oxygen than from nitrogen.

**Table 2-7**

*Ionization energies of the elements in the second period*

| Element | Li | Be | B | C | N | O | F | Ne |
|---|---|---|---|---|---|---|---|---|
| Neuclear charge | +3 | +4 | +5 | +6 | +7 | +8 | +9 | +10 |
| Valence shell | $2s^1$ | $2s^2$ | $2s^2\,2p^1$ | $2s^2\,2p^2$ | $2s^2\,3p^3$ | $2s^2\,2p^4$ | $2s^2\,2p^5$ | $2s^2\,2p^6$ |
| I.E. (kJ $mol^{-1}$) | 520 | 900 | 800 | 1086 | 1403 | 1314 | 1681 | 2081 |

2. **The ionization energy decreases progressively down a group of elements**. The ionization energies of group IA elements are listed in table 2-8. Succeeding elements down the group have increasing atomic radii corresponding to the increasing number of electron shells. The outer electron (*i.e.*, the electron to be

removed) is therefore less firmly held due to increasingd istance from the nucleus and the 'shielding' or 'screening' effect* of the inner electron shells. Hence, the succeeding elements down the group have smaller ionization energies.

Table 2-8 *Ionization energies of group IA elements*

| Element (Symbol) | Atomic number | Electronic configuration | Number of electron shells | I.E. (kJ mol$^{-1}$) |
|---|---|---|---|---|
| Li | 3 | $1s^2$; $2s^1$ | 1 | 520 |
| Na | 11 | $1s^2$; $2s^2$; $2p^6$; $3s^1$ | 2 | 495 |
| K | 19 | $1s^2$; $2s^2$; $2p^6$; $3s^2$, $3p^6$; $4s^1$ | 3 | 418 |
| Rb | 37 | $1s^2$; $2s^2 2p^6$; $3s^2 3p^6 3d^{10}$; $4s^2 4p^6$; $5s^1$ | 4 | 403 |
| Cs | 55 | $1s^2$; $2s^2 2p^6$; $3s^2 3p^6 3d^{10}$; $4s^2 4p^6 4d^{10}$;<br>$5s^2$ $5p^6$; $6s^1$ | 5 | 374 |

3. **Ionization energies of inert gases (He, Ne, Ar, Kr, Xe) are exceptionally high.** This is because it requires a very large amount of energy to remove an electron from a stable valence shell ($1s^2$, in the case of helium; $ns^2np^6$, in others).

4. **The ionization energy sharply drops from an inert gas to the succeeding alkali metal.** For example, the I.E. of Ne is 2081 kJ mol$^{-1}$, of Na, 540 kJ mol$^{-1}$. This is because of the strong shielding effect of an additional electron shell in the alkali metal atom.

5. **The second ionization energy is much higher than the first ionization energy** as the electron is being removed from a positively charged ion, $M^+$, formed by the loss of an electron. In general, the successive ionization energies $IE_1$, $IE_2$, $IE_3$,.... etc. vary in the order $IE_1, < IE_2 < IE_3 < IE_4 ...$, etc,, since the charge of the positive ion formed rises as the number of removed electrons increases, and so its attraction for the remaining electrons.

It is noteworthy that elements with first ionization energy below 940 kJ mol$^{-1}$ are usually metals, those with values above 1000 kJ mol$^{-1}$ are non-metals, and those with intermediate values are metalloids.

**8-1. Measurement of ionization energy.** The element, in the gaseous or vapour state, is introduced at a very low pressure (0·3 mm or less) in a discharge tube. Initially, the amount of current flowing through the tube is almost zero. The voltage across the electrodes is then gradually increased. At a certain voltage, the atoms in the gas ionize and there is a sudden spurt in the current flow. This voltage is called the *ionization potential*. It is expressed in volts and is numerically equal to the ionization energy in electron-volts (eV).

## 9. Electron Affinity

When a neutral atom acquires additional electrons, it forms a negative ion. *The amount of energy released when an electron is*

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*Each outer electron is shielded from the nucleus by the electrons in the inner shells, whereby the effective nuclear charge is reduced. This is described as the 'shielding' effect or 'screening' effect of the inner electron shells.

*added to a neutral gaseous atom is called electron affinity.* That is, it is the energy released* in the change.

$$X(g) + e^- \rightarrow X^-(g)$$

Electron affinities depend on the atomic radii and the *effective* nuclear charge taking into consideration the shielding effect of the inner electron shells. In general, succeeding elements across the periods have higher electron affinities whereas those down the groups have smaller electron affinities. The halogens (F, Cl, Br, I) have high electron affinities (Table 2-9), since the addition of one electron to their atoms results in a stable outer shell consisting of $s^2p^6$ electrons. Among halogens, fluorine does not fit the general trend and has lower electron affinity than chlorine; the succeeding halogens have progressively lower electrons affinities.

Table 2·9. *Electron affinities of group VIIA elments (the halogens)*

| Element | Atomic number | Electron affinity (kJ mol$^{-1}$) |
|---|---|---|
| F | 9 | 333 |
| Cl | 17 | 348 |
| Br | 35 | 340 |
| I | 53 | 297 |

It is noteworthy that the electron affinities of metals are small and their atoms have little tendency to pick up electrons and form negative ions. Non-metals have large electron affinities and readily form negative ions. The concepts of ionization energy and electron affinity are helpful in understanding the formation of compounds from atoms of metallic and non-metallic elements.

## 10. Electronegativity

*The power of an atom to attract to itself electrons in a covalent bond is called the electronegativity of that atom.* The electronegativity of an atom is related in a general way to both its ionization energy and electron affinity and may be taken as the average of the two.

In the periodic table the electronegativity of elements increases across the period with increasing nuclear charge (atomic number) and decreasing atomic radius. Thus in the C—N bond, nitrogen being more electronegative attracts the shared electrons more towards itself. Thus is shown by writing this bond as $\overset{+\delta}{C}—\overset{-\delta}{N}$ or as $\overrightarrow{C—N}$. The most electronegative elements are found towards the end of the periods; these elements also have large ionization energies and large electron affinities. The most electropositive elements, *i.e.*, those with low electronegativities (small

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*In some cases (e.g., Ca, Zn, etc.), energy is absorbed and the electron affinities have negative valves.

Ionization energies and almost zero electron affinities) are found at the beginning of the periods.

In moving downward through the group, the electronegativity of elements progressively decreases in spite of increasing nuclear charge. This is because the increase in atomic radius and the shielding effect of inner electron shells more than compensates the effect of increased nuclear charge. Thus, chlorine is more electronegative than iodine as a result of which the ICI (iodine chloride) molecule develops a partial ionic character, $\overset{+\delta}{\mathrm{I}}\text{—}\overset{-\delta}{\mathrm{Cl}}$ or $\overset{\longrightarrow}{\mathrm{I\text{—}Cl}}$.

**Table 2-10** *Electronegativities : trends in variation*

| | | | | | | |
|---|---|---|---|---|---|---|
| Li (1·0) | Be (1·5) | B (2·0) | C (2·5) | N (3·0) | O (3·5) | F (4·0) |
| Na (0·9) | | | | | | Cl (3·0) |
| K (0·8) | | | | | | Br (2·8) |
| Rb (0·8) | | | | | | I (2·4) |
| Cs (0·7) | | | | | | |

## 11. Metallic/Non-metallic Properties

Metals are characterized by a marked tendency to lose valency electrons and form positive ions when they enter into combination with other elements, *e.g.*, $M \rightarrow M^+ + e^-$. This tendency increases with increasing atom size and decreasing ionization energy, electron affinity, and electronegativity. The metallic properties, therefore, weaken across the periods but become more pronounced with each succeeding element down a group. Thus, while groups IVA, VA, VIA, and VIIA are headed by the non-metals carbon, nitrogen, oxygen, and flourine respectively, they end up with lead, bismuth, polonium, and astatine respectively all of which exhibit metallic properties, at least to some degree.

Non-metals possess a relatively high electron attracting power and large ionization energies, and do not tend to form positive ions during chemical changes. The non-metallic properties, therefore, become more pronounced in succeeding elements across the periods but weaken progressively down the groups.

**11-1. Nature of Oxide** In general, metals form basic oxides; non-metals from acidic oxides. Therefore, in any period, the nature of the oxide varies from strongly basic through amphoteric or neutral to strongly acidic. This is shown below for the elements of the third period.

**Table 2-11.** *Nature of oxides of the elements of third period*

| Elements→ | Na | Mg | Al | Si | P | S | Cl |
|---|---|---|---|---|---|---|---|
| Oxides→ | $Na_2O$ | MgO | $Al_2O_5$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $Cl_2O_7$ |
| Nature of oxides→ | strongly basic | basic | amphoteric | feebly acidic | acidic | strongly acidic | very strongly acidic |

Down the group, the basic character of the oxide becomes progressively stronger and the acidic character progressively weaker. Thus, in group IIA (Be, Mg, Ca, Sr, Ba), the hydroxides of Be and Mg are only feebly basic while $Ba(OH)_2$ is very strongly basic; in group VIIA (F, Cl, Br, and I), the oxide of iodine is the least acidic or the most strongly basic.

## 12. Strength as oxidizing/reducing agent

Oxidizing agents are characterized by the tendency to take up electrons and reducing agents by their tendency to give up electrons during chemical reactions. Thus elements with high ionization energies, electron affinities, and electronegativities are oxidizing agents; those with low ionization energies, etc. are reducing agents.

In general, the strength as oxidizing agent of elements progressively increases across the periods and decreases down the groups. The reducing strength of elements is progressively lower across the periods and higher down the groups. Thus, fluorine should be the strongest oxidizing agent and francium the strongest reducing agent of all the elements.

## 13. Summary of Trends in the variation of Properties in the Periodic Table

### 1. Across the periods

(*i*) Number of valency electrons increases from 1 to 8.
(*ii*) Number of electron shell remains unchanged.
(*iii*) Atomic radius (size of the atoms) decreases.
(*iv*) Ionization energy, electron affinities, and electronegativity increase.
(*v*) Strength as an oxidizing agent increases.
(*vi*) Strength as a reducing agent decreases.
(*vii*) Metallic character and the basicity of oxides decrease.

### 2. Down the groups

(*i*) Number of valency electrons remains the same— equal to the group number from groups 0 to VIII.
(*ii*) Number of electron shells increases progressively.
(*iii*) Size of the atoms increases.
(*iv*) Ionization energy, electron affinity, and electronegativity decrease.
(*v*) Strength as an oxidizing agent decreases.
(*vi*) Strength as a reducing agent increases.
(*vii*) Metallic character and the basicity of oxides increase.

## 14. Superiority of Long Form Periodic Table

The long form periodic table is superior to the older short form tables in the following respects :

1. This table corresponds to the arrangement of electrons

in the atoms of the elements. Thus each vertical column represents a family of elements with similar electronic configurations and similar properties.

2. It explains the similarities and variations in the properties of the elements in terms of their electronic configurations and brings out clearly the trends in chemical properties across the long periods.

3. The inert gases having completely filled electron shells come at the end of the periods which represents a logical completion of each period.

4. It avoids the confusion arising from the juxtaposition of the dissimilar A and B sub-groups. The elements constituting A sub-groups (IA, IIA....... VIIA) have only their outer shell incomplete while all the inner shells are complete. These are the **normal elements**. The elements of B-subgroups (IB, IIB.......VIIB) and group VIII have their last two shells incomplete. These are the **transitional elements**.

5. It provides satisfactory positions to the elements of group VIII in three separate vertical columns.

6. It shows the main groups of elements, *e.g.*, non-metals, active metals, transition metals, lanthanides, actinides, and inert gases clearly demarcated. The non-metal elements are placed at the right of the table while the metals are at the left. The active metals are located at the extreme left (groups IA and IIA) while the transition metals are found in the middle of the table (groups IIIB to IIB).

On the basis of their electronic configurations, the elements have been grouped as *s*-block, *p*-block, *d*-block, and *f*-block elements, all the four blocks being clearly demarcated in the long form periodic table.

7. It is easier to remember, understand, and reproduce.

## 15. Blocs of Elements in the Periodic Table

In addition to the periodic relationships, there are some general aspects of chemical behaviour that depend on what *type* of electrons are there in the valence shell. On the basis of the types of electrons in the valence shell, the elements in the periodic table can be divided into four blocs : the *s*-bloc elements, the *p*-bloc elements, the *d*-bloc elements, and the *f*-bloc elements.

**1. The *s*-blod elements.** These are the elements in which the last electron enters an *s*-sub-shell*. Since an *s*-shell can have either one electron or two electrons, the outer shell configuration

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*The statement that the *s*-block elements are those in which the atoms have only *s*-electrons in the outer shell is not wholly correct, since this definition will include the elements of B-subgroups also.

of *s*-block elements is either $ns^1$ or $ns^2$. The elements of $ns^1$ ending constitute group IA (the alkali metals—Li, Na, K, Rb, Cs, and Fr) and those of the $ns^2$ ending, group IIA (the alkaline earth metals—Be, Mg, Ca, Sr, Ba, and Ra).

The *s*-bloc elements are highly reactive. They are characterized by low ionizations energy and readily form positive ions in chemical combinations.

**2. The *p*-bloc elements.** These are the elements in which the last electron enters a *p*-subshell. Since, a *p*-subshell starts filling after the *s*-subshell has been filled, the outer shell configurations of the *p*-bloc elements vary from $ns^2\ np^1$ to $ns^2\ np^6$. The *p*-bloc elements constitute group IIIA ($ns^3\ np^1$ ending), group IVA ($ns^2\ np^2$ ending), group VA ($ns^2\ np^3$ ending), group VIA ($ns^2\ np^4$ ending), group VIIA ($ns^2\ np^5$ ending), and the 0 group ($ns^2\ np^6$ ending). The elements of the zero group are characterised by extreme chemical inactivity.

The elements of the *s*- and the *p*-blocs are called *representative elements.* However some scientists prefer to categorize the zero group of inert gases as a different type of elements rather than as representative elements.

**3. The *d*-bloc elements.** Elements in which the last electron enters the *d*-subshell while the *s*-subshell of a higher level has already received two electrons are called the *d*-bloc elements. They make up three complete rows of 10 elements each and an incomplete fourth row in the long periodic table beginning with group IIIB and continuing through group IIB. The electronic configuration for the two outer shells of these elements can be represented as $(n-1)d^{1-10}\ ns^{1-2}$. The *d*-bloc elements are also called *transition elements*. The transition metals make four distinct series :

The *first transition series* (Sc, at. no. 21, to Zn, at. no. 30) begins with scandium which has only 1 electron in the 3*d* level. The extra electrons in the successive nine elements enter the 3*d* level which continues to expand until the number of electrons in it reaches ten at copper when the series is completed The *second transition series* runs through yttrium (at. no 39) to cadmium (at. no. 48) and the *third transition series* through lanthanum (at. no. 57) to mercury (at. no. 80), and have incomplete 4*d* and 5*d* levels respectively. The *fourth transition series* begins with actinium (at. no. 89) and is characterized with an incomplete 6*d* level.

**4. The *f*-bloc elements.** These are elements in which the last electron enters the *f*-subshell of the third level from the outer side of the atom. They not only have incomplete *d*-subshell in the penultimate shell (second from the outer side) like the transition elements but also incomplete *f*-level in the next inner one. Their outer electron configurations are $(n-2)\ f^{1-14}$, $(n-1)\ d^{0-2}$, $ns^2$. They occur within the transition series of the sixth and seventh periods and for this reason, are also called the *inner transition elements.* There are two series of these elements :

(*i*) *The lanthanide series.* (at. no. 58 to 71) in which the number of elctrons progressively increases in the 4*f* orbitals.

(*ii*) *The actinide series* (at. no. 90 to 103) in which the number of electrons progressively increases in the 5*f* orbitals.

Elements of each one of these series are very much similar in their chemical properties because of the identical configurations of the outer two shells. For this reason each group of these elements is placed together as a single element with lanthanum (at. no. 57) and actinium (at. no. 89) respectively and detailed out separately outside the main periodic table.

The *d*-and *f*-bloc elements are somewhat out of line in the trends in the variation in atomic radii of elements. Thus, there is a slight increase in atomic radius toward the end of the transition series in periods 4, 5, and 6, which results from the shielding of the outermost electrons as the underlying *d* sublevels are filled.

**15-1. General characteristics of transition metals or *d*-bloc elements**. Transition elements of all the four series (3*d*, 4*d*, 5*d*, and 6*d*) exhibit following general characteristics :

1. *Physical properties.* They are all metals with high densities and high melting and boiling points. They are hard, ductile, and good conductors of heat and electricity. Zinc, cadmium, and mercury are notable exceptions.

2. *Ionization energy.* Their ionization energies are, in general, midway between those of the *s*-bloc and *p*-bloc elements.

3. *Variable valency.* Transition elements have generally two electrons (in a few cases, one electron) in the outer level and a varying number of unpaired *d* level electrons in the second outer shell. The unpaired *d* electrons have about the same energy as the *s*-electrons of the outer shell. So, one or two *d* electrons are readily involved along with the outer *s* electrons for chemical bonding. Hence, transition elements exhibit various positive valences in their compounds.

4. *Colour.* Transition metal ions with incomplete inner shells are usually coloured, both in solid salts and in solutions. By absorbing energy as light in the visible region, *d* electrons in the transition metals are promoted to a higher energy level in the *d* sub-shell itself and light of a different colour is transmitted. In normal elements, electron is to be promoted to an outer shell for which much energy is required. The light is, therefore, absorbed from ultraviolet region and no colour is shown.

The colour exhibited depends upon the oxidation state of the metal as indicated by the following examples : $Fe^{2+}$ (green), $Fe^{3+}$ (yellow); $Cr^{2+}$ (blue), $Cr^{3+}$ (green); and $Mn^{2+}$ (pink), $Mn^{3+}$ (violet).

5. *Paramagnetism.* Most of the transition elements are attracted by magnetic fields, a property called paramagnetism. It results from the presence of unpaired electrons in the system (atom or ion). The magnetic field induced about an electron spinning on its axis either clockwise or anti-clockwise remains uncancelled if it is not paired by an electron spinning in opposite direction. Hence, unpaired electrons produce unbalanced magnetic fields in atoms causing them to be *paramagnetic*. The greater the number of unpaired electrons, the greater is the paramagnetism.

## 16. Usefulness of the Periodic Table

In spite of certain imperfections, the periodic table has been of great value in the advancement of chemistry. The usefulness of periodic table may be evaluated under the following headings :

**1. Classification of elements**. The periodic table is the most successful system of classifying elements. It presents much useful information about the elements and the trends in the variations of their properties in a convenient, compact form. It simplifies the study of chemistry by grouping together the elements with similar properties. Thus, it is sufficient for a general study to learn the properties of eace group rather than the properties of each element separately.

**2. Prediction of properties of elements**. The periodic table enables one to make reasonably reliable predictions regarding the properties of any element by comparison and correlation with the properties of those situated below, above, to the left, and to the right of it. Thus, tit is a valuable aid in learning the chemistry of such elements which cannot be isolated in measurable quantities. *e.g.*, astatine, francium, etc.

By way of example, consider astatine with the atomic number 85. It is located in group VIIA below iodine. It would probably be a solid at ordinary temperatures, since iodine just above it is a solid, and the trend is from gas to liquid to solid going down the group. Since the colour of group VIIA elements darkens moving downward, this element would probably be dark or black in colour, with a metallic lustre like iodine. The element would combine with sodium to form a white, crystalline compound soluble in water, and corresponding to the formula NaAt since the members of the family form similar compounds with sodium. It would be fairly active element chemically but less active than iodine since the trend is towards decreasing chemical activity as one goes down the group.

**3. Stimulation to research**. Periodic table is a valuable guide in chemical and metallurgical researches as it summarises the properties of elements. It was from a close study of the periodic table that the element fluorine was picked up for the preparation of a non-inflammable and non-toxic refrigerant. The result of the research was Freon ($CF_2Cl_2$). a very successful refrigerant. Metallurgists study the periodic table for selecting elements that would give an alloy possessing required physical and chemical properties.

Uses of the periodic table of historical interest are :

4. **Correction of atomic weights.** In many cases, two consecutive elements were found to differ from the members of their groups unless their positions in order of their atomic weights in the table were reversed. This caused a suspicion about the correctness of the accepted atomic weight of either. This led to a check-up of atomic weights and many errors were corrected.

5. **Prediction of undiscovered elements.** While compiling the original periodic table, many gaps had to be left so that elements could be placed below those with similar properties. These gaps corresponded to the elements as yet undiscovered. By correlation and comparison with the neighbours on the right and the left, above and below, Mendeleef predicted not only the existence of such elements but also their general physical and chemical properties. When these elements were actually discovered and their properties studied, these predictions were found to be remarkably accurate.

## Questions

1. (*a*) State the modern Periodic Law and explain its meaning.

(*b*) Give the meaning of the following terms as applied to the Periodic Table : group, period, short period, long period.

2. Explain the statement, "the periodicity in properties of elements is a reflection of the periodicty of electron configurations".

3. The number of elements in the first period of the periodic table is 2, in the second and third periods is 8 each, in the fourth and fifth is 18 each, and in the sixth period is 32. Explain why this is so.

4. Write the valence shell electron configurations of—

(*i*) the elements of group IIIA,
(*ii*) the elements of group VIIA,
(*iii*) the inert gases,
(*iv*) the transition elements, and
(*v*) the lanthamides.

5. Discuss the trends in the variation of atomic radii in the periodic table.

6. What is atomic volume ? What is the importance of the values of atomic volumes in the study of the atomic radii ?

7. Explain the reason why positive ions are always smaller than the parent atom while the negative ions are always larger than the parent atom.

8. (*a*) Define the term ionization energy. Give the units in which it is measured, and the interrelationship of different units.

(*b*) Discuss the general trends in the variation of ionization energies in the periods table.

9. (*a*) Which of the following electron configurations would you expect to have the lowest ionization energy, and why ?

(*i*) $1s^2, 2s^2\ 2p^6, 3s^1$ (*ii*) $1s^2, 2s^2\ 2p^5$ (*iii*) $1s^2, 2s^2\ 2p^6$

(*b*) The ionization energy of hydrogen is 1310 kJ $\text{Mol}^{-1}$ and of the very next element, helium, 2359 kJ $\text{Mol}^{-1}$. Explain the large increase in the ionization energy from H to He.

10. Define electron affinity. How does it vary across the periods and down the groups in the periodic table ?

11. Define electronegativity. Describe the general trends in the variation of electronegativities in the periodic table.

12. Relate (*a*) metallic/non-metallic character of elements and (2) strength of elements as oxidizing/reducing agent to ionization energy, electron affinity, and electronegativity.

13. The chemical reactivity of the elements of Group IA increases downward while that of the elements of Group VIIA decreases downward. Explain the difference.

14. Describe in brief the superiority of the long form periodic table over the older short form tables.

15. Give a brief, explanatory account of the various blocks of elements in the periodic table.

16. Write an explanatory note on the usefulness of the periodic table.

17. Describe the general features of the transition elements.

18. Explain :

- (*a*) The ionization energy of boron (at. no. 5) is less than that of the preceding element beryllium (at. no. 4).
- (*b*) The second ionization energy of atoms is higher than the first ionization energy.
- (*c*) The elements in the same group of the periodic table show close resemblance in chemical behaviour.
- (*d*) Lanthanides (atomic numbers 57-71) show close resemblance in chemical behaviour.
- (*e*) Transition elements are paramagnetic while the normal elements are not.
- (*f*) Transition elements show variable valency.
- (*g*) Inert gases display almost total lack of chemical activity.

19. The following represents a period from the Periodic Table with hypothetical symbols for the elements :

| Group → | IA | IIA | IIIA | IVA | VA | VIA | VIIA | O |
|---|---|---|---|---|---|---|---|---|
| Element → | A | B | C | D | E | F | G | H |

(*a*) Which of these elements will be
- (*i*) most metallic,
- (*ii*) most non-metallic,
- (*iii*) most unreactive,
- (*iv*) strongest oxidizing agent,
- (*v*) strongest reducing agent ?

(*b*) Write the formula for the compounds formed by the union of
- (*i*) A and F
- (*ii*) B and G
- (*iii*) B and E
- (*iv*) D and G.

20. An element X has three electron shells, with five electrons in the outermost shell. Predict the following about the element :

- (*i*) The period in which it will fall.
- (*ii*) The group in which it will fall.
- (*iii*) Its atomic number.
- (*iv*) Whether it will be a metal or a non-metal.
- (*v*) Formula of its compound with hydrogen.

21. Without looking at the Periodic Table, select from each of the following lists of atomic numbers (N) the elements which belong to the same group (or sub-group) :

(*a*) 3, 17, 19, 50, 55
(*b*) 4, 12, 30, 56, 98
(*c*) 6, 10, 14, 40, 60

22. Name the following :

(*a*) The most electropositive element.
(*b*) The most electronegative element.
(*c*) The elements of group IA.
(*d*) The elements of group VIIA.
(*e*) The naturally occurring element, with the highest atomic number.

23. Distinguish between :

(*i*) Transition elements and normal elements.
(*ii*) Transition elements and inner transition elements.
(*iii*) Lanthanides and actinides.

24. Which of the following are transition elements :

(*a*) K, Mn, Ca, Cs, Fe, Pt
(*b*) Cr, Ca, Cu, Cl, Co ?

25. Some one claimed to have discovered an element which fits in between hydrogen (at. wt. = 1) and helium (at. wt. = 4) in the Periodic Table. Comment upon this claim.

## Key

4. (*i*) $ns^2, np^1$ (*ii*) $ns^2 np^5$ (*iii*) $ns^2 np^0$ (*iv*) $(n\text{-}1)\, d^{1-10}, ns^{1-2}$
(*v*) $(n\text{-}2)\, f^{1-14}, (n\text{-}1)\, d^{0-2}, ns^2$

9. (*a*) The electron configuration $1s^2, 2s^2\, 2p^5, 3s^1$ will have the lowest ionization energy as the electron to be removed ($3s^1$) is farthest away from the nucleus, being in the third level; in other configuration the electron is in the second level.

(*b*) The nuclear charge of helium (= 2) is double that of hydrogen (= 1); hence the electrons in the 1*s* shell of helium are held more tightly.

13. The chemical reactivity of group IA elements having one 1 electron in the outermost shell depends on their ionization energy which increases downward the group. The chemical reactivity of the elements of group VIIA elements having 7 electrons in the outermost shell depends upon their electron affinity and electronegativity which decrease downward the group.

17. (*a*) Ionization of boron ($1s^2, 2s^2\, 2p^1$) involves the removal of a *p* electron in the second level while that of beryllium ($1s^2, 2s^2$) involves the removal of an *s* electron in the same level. In any level, the energy of a *p* electron is higher than that of an *s* electron.

(*b*) Second ionization energy is related to the removal of an electron from the positive residue $M^+$ formed by the removal of an electron from the neutral atom M.

(*c*) They have the same number of valence electrons.

(*d*) They have identical electron configuration in the outer two levels.

(*e*) A single unpaired electron produces a magnetic field in much the ame way as an electric current in a conductor creates a magnetic field around he conductor. If two electrons are paired in the same orbital, their magnetic effects cancel out. Therefore, transition elements with unpaired elements are paramagnetic, while normal elements with all paired electrons are diamagnetic.

(*f*) Transition elements can involve the *d* electrons of the second outer shell which have about the same energy as the *s* electrons of the outermost shell.

(*g*) Inert gases have the most stable electron configuration, $ns^2\ np^6$, in the outermost level. Hence, they do not have any tendency to lose, gain, or share their valency electron.

19. (*a*) (*i*) A (*ii*) G (*iii*) H (*iv*) G (*v*) A

(*b*) (*i*) $A_2F$ (*ii*) $BG_2$ (*iii*) $B_3E_2$ (*iv*) $DG_4$

20. (*a*) (*i*) Third period (number of electron shells = 3).

(*ii*) Group V (number of electrons in outermost shell = 5).

(*iii*) 15 (At. No. = total number of orbital electrons. In the case of this element, the 1st shell has 2, the 2nd shell 8, and the 3rd shell has 5 electrons; hence the total number of electrons $= 2+8+5 = 15$).

(*iv*) non-metal (number of electrons in the third and the outermost shell is more than 4).

(*v*) $XH_3$.

21. (*a*) 3 and 19; (*b*) 12 and 56, (*c*) 6 and 14.

22. (*a*) Francium, (*b*) Fluorine, (*c*) Alkali metals, (*d*) Halogens, (*e*) Uranium.

24. (*a*) Mn, Fe, Pt; (*b*) Cr, Cu, Co.

25. The claim is absurd; the at. no. of H is 1 and that of He is 2. Hence, there can be no element between H and He.

□□

## 3

# Phase Equilibria

The three states of matter are often referred to as the gas phase, the liquid phase, and the solid phase. A heterogeneous equilibrium is an equilibrium between two or more phases, such as the equilibrium between a liquid and its saturated vapour, between a saturated solution and excess of solute, between the mixtures of miscible, partially miscible, or immiscible liquids, the distribution of a solid or liquid between two liquids, etc. The knowledge of heterogeneous equilibria, which are all governed by Gibb's phase rule, has many important applications such as fractional distillation, crystallilization, extraction of a solute with a second solvent, chromatography, etc.

## 1. The Phase Rule

Two or more *different* phases in equilibrium with one another constitute a heterogeneous equilibrium. Such a system is governed by the important generalization called Gibb's phase rule. Before stating this rule, the technical terms involved in it must be explained. These terms are : system, phase, component, and degree of freedom.

**1-1. System**. A system refers to a part of space filled with a substance or mixture of substances and isolated from the surrounding medium. It may include only one phase or more than one phases. A *homogeneous system* is one in which only a single phase is present. Mixtures of gases, liquid water, and solutions are all examples of homogeneous systems. A *heterogeneous system* is one which consists of two or more phases, *e.g.*, water—ice—water vapour (the number of phases=3), water—oxygen—nitrogen (the number of phases=3), etc.

**1-2. Phase**. A phase is a part of a system which is itself homogeneous (*i.e.*, it has exactly the same physical properties and chemical composition throughout) and is separated from other parts of the system by physical boundaries in the nature of visible surfaces. A phase may be solid, liquid, or gas according to its physical state. For example, if a flask is partially full of water in which ice is floating, the system comprising the contents of the flask consists of three phases—the solid phase ice, the liquid phase water, and the gaseous phase water vapour (Fig. 3-1). A phase in a system comprises of all the parts that have the same properties and composition. Thus, if the system represented in Fig. 3-1 had more than one pieces of ice, it will not have as many solid phases; all the pieces of ice will constitute only one solid phase. That is, *sub-division of a phase does not produce new phases.*

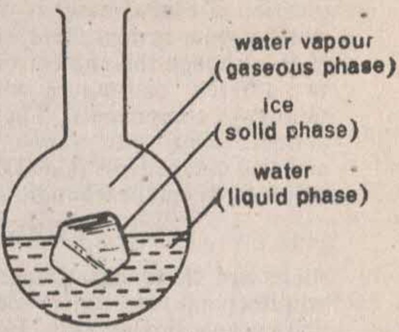

Fig. 3-1. A system consisting of three phases.

A phase may be comprised of an element, a chemical compound, or a homogeneous mixture, *i.e.*, a solution of elements or compounds. A solution of ethyl alcohol and water constitutes a single phase since the two liquids are completely miscible in one another and make a single liquid solution (Fig. 3-2). The same is true of a mixture of gases, no matter how many gases are present, and of an unsaturated solution of a solid in a liquid. A system of ether and water has two phases since the two liquids are not perfectly miscible and separate in two layers with a definite bounding face between the two (Fig. 3-3), the upper layer of ether and the lower one of water. A saturated solution of sodium chloride in equilibrium with undissolved solid constitutes two phases; the saturated solution is the liquid phase and the undissolved solid is the solid phase. A mixture of solids, except when a solid solution is formed, consists of as many different phases as the number of solids present, and *every solid allotropic form constitutes a separate phase.*

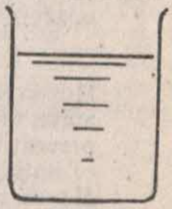

Fig. 3-2. A solution of ethyl alcohol and water—one single phase

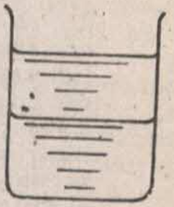

Fig. 3-3. A system of ether and water—two phases.

In a heterogeneous equilibrium, the various phases of the system are in *dynamic equilibrium* with one another. Since the container is never in dynamic equilibrium with the phases of a system, it does not constitute a phase of the heterogeneous equilibrium.

**1-3. Component.** The simple substances from which phases can be built are known as components. The number of components in a system is the smallest number of such substances which must be specified to be present in order to describe completely the composition of every phase of the system Thus, in the ice—water—water vapour system there is only one component, namely water, $H_2O$, although the number of phases is three. A system containing two different substances which do not react with each other contains two components. Thus, a solution of ethyl alcohol in water, in equilibrium with vapour has two phases (liquid and gaseous) and two components ($C_2H_5OH$ and $H_2O$). In the thermal decomposition of calcium carbonate

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

there are three constituents and three phases in heterogeneous equilibrium, *viz.*, solid sodium carbonate, solid calcium oxide, and carbon dioxide gas. However, once the concentration of any two of the three substances is specified, the concentration of the third one is also fixed. Therefore, the number of components of this system is two, and we can select any two of the constituents as the components.

In the thermal dissociation of ammonium chloride, there are two phases present, *viz.*, solid ammonium chloride and the gaseous mixture of ammonia and hydrogen chloride :

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

However, the gaseous mixture consists of the constituents of ammonium chloride in the same proportion in which they are present in the solid ammonium chloride. Thus, the composition of both phases can be represented by the same individual, $NH_4Cl$. Hence, it is a one-component system.

The foregoing examples make it clear that the term 'components of a system' does not mean the various constituents or chemical individual present in the system

**1-4. Degree of freedom.** *The number of degrees of freedom of a system* is the minimum number of factors such as pressure, temperature, and concentration of the various components which can be varied independently of each other without bringing about a change in the number of phases. For example, in the system *water$\rightleftharpoons$steam*, once one of the two variables temperature and pressure is fixed, the other is also settled. The alteration of either of these factors will cause one of the phases to disappear. This system therefore, has only one degree of freedom and is said to be *univariant*. In the system ice$\rightleftharpoons$water$\rightleftharpoons$water vapour, the three phases can be in equilibrium only at one definite temperature and pressure. The number of degrees of freedom of the system is zero and the system is said to be *invariant*. A system having two degrees of freedom is said to be *bivariant*.

**1-5. Phase rule.** We are now in a position to state the phase rule which was devised by Gibbs in 1876. According to this rule—

*"For a heterogeneous system in equilibrium, the number of degrees of freedom is equal to the difference between the numbers of components and phases, plus two."*

Expressed in symbols,

$$F=C-P+2$$

Here, F is the number of degrees of freedom for the equilibrium. C is the number of components for the system, and P is the number of different phases in equilibrium with one another. The number 2 on the right is for the two additional variables of temperature and pressure besides the concentration variable.

**1-5. Equilibrium.** Phase rule applies to system in true equilibrium *A true equilibrium is said to exist in a system under a given set of conditions when the same state can be attained by following any possible procedure* For example, at 1 atmosphere pressure the temperature of the system ice-liquid water in equiliprium will be 0°C whether the equilibrium is attained by partial *freezing* of water or by partial *melting* of ice. Therefore, the system exists in true equilibrium.

By careful cooling, it is possible to cool water below its freezing point, 0°C—say to —1°C. But it is not possible to obtain water at —1°C by melting ice. Hence, though water can exist at —1°C, it is not in true or stable equilibrium at this temperature but is in a state of *metastable* equilibrium. When the water at —1°C is stirred or a crystal of ice is added it, solidification sets in and the temperature rises to 0°C.

## ONE COMPONENT SYSTEMS

## 2. Liquid-vapour Equilibria

**2-1. Evaporation.** At any given temperature, the molecules of a liquid have a constant average kinetic energy. They do not all have the same kinetic energy, however, some have lower energies, some have higher. The molecules with sufficiently high kinetic energies overcome the attraction of the neighbouring molecules and escape, *i.e.*, *evaporate*, into the space above the liquid. (Fig. 3-4 *a*). This phenomenon is called evaporation. As the temperature of a liquid is increased, more of the molecules come to have sufficient energy to escape and thus the rate of evaporation increases.

Though it is the fast-moving molecules which evaporate from a liquid, the vapour formed is certainly not at a higher temperature than the liquid. This is because the excess energy of the evaporating molecules is used up in overcoming the inter-molecular attractions in the liquid. However, since the escaping molecules have a higher kinetic energy than the average, the remaining molecules will have a lower average kinetic energy and therefore a lower temperature. Evaporation is thus a cooling process. The evaporating liquid, however, remains at a constant temperature since it absorbs heat from the surroundings.

**2-2. Vapour pressure**. If a liquid is placed in a closed container, its molecules escaping into the gas phase strike the container and rebound. Some of the rebounding molecules strike the surface of the liquid where they are trapped [Fig. 3-4 (*b*)]. The return of the molecules from the gas phase to the liquid phase is termed *condensation*. As evaporation proceeds, the number of molecules in the gas phase increases and, in turn, the rate of condensation increases. After a short while, the rate of condensation will become equal to the rate of evaporation. When this happens, the vapour inside the closed container will be in a dynamic equilibrium* with its liquid :

$$\text{Liquid} \underset{\text{condensation}}{\overset{\text{evaporation}}{\rightleftharpoons}} \text{Vapour}$$

At this equilibrium the space above the liquid is saturated with respect to the molecules in the gas phase. *The pressure exerted by the vapour, i e., the molecules in the gas phase in equilibrium with its liquid at a given temperature is called the vapour pressure of the liquid at that temperature.* The vapour pressure does not depend upon the quantity of liquid present, the area of its surface, or the volume of the vapour. It, however, depends upon the temperature and the nature of the liquid (polar liquids, *e.g.*, ether and ethyl alcohol, with weaker forces of attraction between their molecules, have higher vapour pressure than more polar liquids, *e.g.*, water).

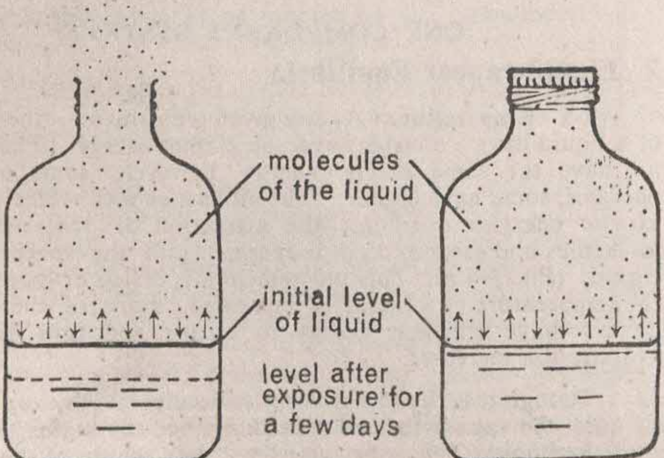

Fig. 3-4. (*a*) Molecules of liquid can escape from the open container, and evaporation occurs. (*b*) Molecules of liquid do not escape from the closed container and dynamic equilibrium occurs.

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*The equilibrium which is established with the opposing changes, *e.g.*, evaporation and condensation, involved being in full operation and balanced is called dynamic equilibrium

**2-3. Vapour pressure and temperature.** As the temperature increases, the vapour pressure increases. This is due to an increase in the kinetic energy of the molecules or the rate of molecular motion with an increase in temperature. The result is a more rapid escape of molecules from the surface of the liquid and thus a higher equilibrium vapour pressure.

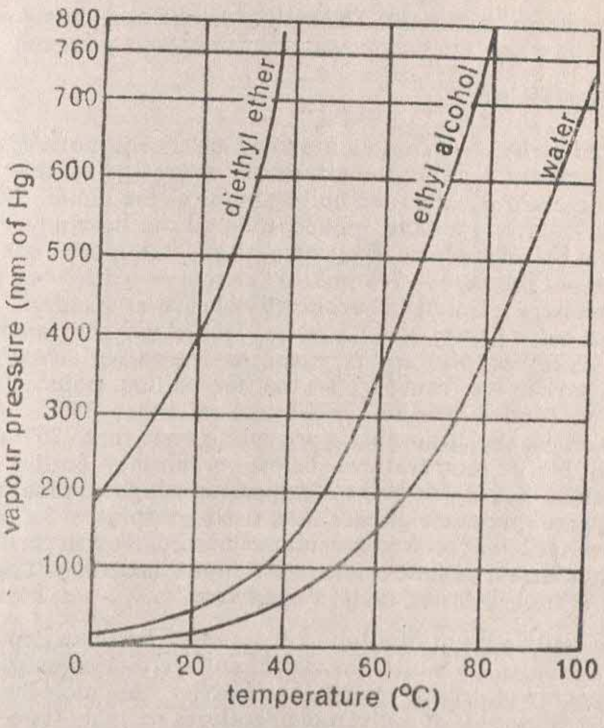

Fig. 3-5. Vapour pressure temperature curves for water, ethyl alcohol, and ether.

The influence of temperature variation upon vapour pressure is represented in Fig. 3-5, which is a curve comparing vapour pressure at various temperatures for the very polar liquid water to the much less polar liquid ethyl alcohol and the still less polar liquid ether. The curves are all logarithmic, and it will be noted that the increase per degree increases as the temperature rises. At any temperature, however, the vapour pressure of water is lower than that of ethyl alcohol, and that of ethyl alcohol is lower than that of ether.

In the liquid—vapour equilibrium, only one vapour pressure corresponds to each temperature specified. Conversely, if the vapour pressure is specified, there is a corresponding temperature. In both cases, the system has one degree of freedom, and once one variable is specified the other is fixed. The same result can be arrived at by the application of phase rule to the liquid—vapour equilibrium which has two phases and one component. So, the number of degrees of freedom

$$\begin{aligned} F &= C-P+2 \\ &= 1-2+2 \\ &= 1 \end{aligned}$$

and the system is univariant. The system can be completely defined by specifying either the temperature or the vapour pressure.

## 3. Boiling Point

A liquid boils at a temperature at which its equilibrium vapour pressure becomes equal to the external pressure against the liquid. This temperature is called the boiling point of the liquid. Depending on the external pressure applied, a liquid can have any number of different boiling points. For comparison, therefore, one particular external pressure —760 mm of mercury— called one atmospheric pressure (1 atm) is arbitrarily chosen as standard. Thus, the *normal boiling point* of a liquid is defined as *the temperature at which its vapour pressure is equal to 760 mm of mercury*. For example, we can see from Fig. 3-5 that the boiling point of water is 760°C, of ethyl alcohol 78°C, and of ether 35°C. At high altitudes where the atmospheric pressure is less than 760 mm, a liquid will boil at temperatures below its normal boiling point. Conversely, a liquid will boil at temperatures higher than normal under external pressures greater than one atmosphere. In pressure cookers water boils at a temperature higher than normal due to a high equilibrium vapour pressure inside the container. Therefore, the food is cooked faster than in open vessels.

The boiling point of a liquid at standard pressure depends on two main factors, its molecular weight and its molecular structure. The larger the molecular weight the heavier the molecules with lower average speeds at a given temperature; so, the fewer molecules escape from the liquid. This explains the progressive rise in boiling point with rising molecular weight in a homologous series of organic compounds. As to the molecular structure factor, it may be noted that polarity and hydrogen bonding in the molecules cause rise in boiling points.

## 4. Solid—Liquid—Vapour Equilibria

The relation between the solid, liquid, and vapour phases of a given substance can be represented graphically by means of a *phase diagram* of that substance. A phase diagram is developed by plotting pressure against temperature for a single substance.

**4-1. Phase diagram of water.** Fig. 3-6 shows the phase diagram of the water system. This is a one component system, $H_2O$ being the only chemical involved. The three phases taking part in the system are ice (solid), liquid water (liquid), and water vapour (gas). The number of phases that can exist simultaneously depends on the conditions of temperature and pressure.

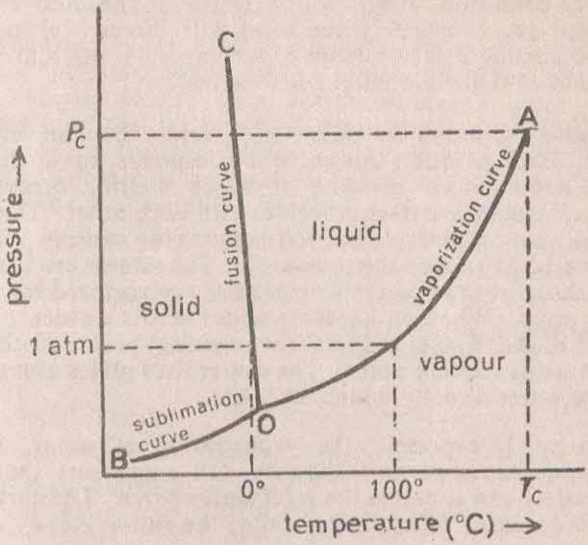

Fig. 3-6. Phase diagram of water.

The curve OA shows the variation of the vapour pressure of water with temperature. Each point on this curve corresponds to a definite pressure and a definite temperature at which boiling occurs, and water and vapour are in equilibrium. As the pressure is increased, the boiling point of water increases until the *critical point* A is reached. Here the boundary between the liquid and vapour states disappears and the densities of the liquid and the vapour become identical. The temperature $T_c$ corresponding to the critical point is called the *critical temperature* (374°C for water). The liquid state cannot exist above the critical temperature, no matter how great the pressure. The pressure $P_c$ corresponding to the critical point is called critical pressure (217·7 atm for water), and it is the minimum pressure that causes the appearance of the liquid state at the critical temperature.

The curve OB, which may be continued to the absolute zero, depicts the variation of the vapour pressure of ice with temperature. The points on the curve OB show the conditions of equilibrium between ice and water vapour. The curves OA and OB meet at the point O. This point lies on the curve OA along which water and vapour can coexist and it also lies on the curve OB along which water and ice can coexist. So, the point O corresponds to the temperature and pressure at which all three states can remain in equilibrium with each other. This point is therefore called the *triple point*. For water, the triple point occurs at 0·01°C and 4·6 mm of Hg (about 0·006 atm). From curve OB it will be noted that if the vapour at some pressure below that if the triple point is cooled sufficiently, the vapour will directly change to solid without forming liquid as an intermediate stage. This represents the condition under which snow is produced in the upper atmosphere. Conversely, the solid will directly change to vapour upon heating if the pressure of the vapour is not allowed to rise above that of the triple point (*sublimation*).

The curve OC shows the effect of pressure on the melting point of ice. Each point on this curve corresponds to a definite temperature and a definite pressure at which melting occurs and ice and water vapour are in equilibrium with each other. The line OC inclines very slightly to the left because the melting point of water is lowered by raising the pressure*. The steepness of the curve OC shows that appreciable pressures are required to reduce the melting point. When an ice skate glides across a sheet of ice, the pressure of the blade reduces the melting point of the ice below the normal melting point. The skater thus glides along on a thin layer of water directly under the blade.

The curve OA represents the vaporization of water, and is called the *vaporization curve*. The curve OB represents the sublimation process and is called the *sublimation curve*. The curve OC represents the melting of ice, and is called the *fusion curve*.

The curves OA, OB and OC divide the phase diagram into three areas, each area corresponding to only one of the three physical state of water. At temperatures and pressures corresponding to points in the area AOC liquid is the only stable phase. Similarly, under the conditions of the area BOA water can exist only as vapour and under the conditions of the area COB water can exist only in the solid phase, *i.e.*, as ice.

**4-2. Significance of areas, lines, and points in the phase diagram.** Each area in the phase diagram represents a particular *bivariant* system corresponding to the existence of a single phase. To define the system at any point within an area it is necessary to specify both the pressure and temperature. Thus any system —vapour, water, or ice—represented by an area has two degrees of freedom. The same conclusion is reached by the application of phase rule : $F=C-P+2=1-1+2=2$.

The lines in the phase diagram represent the conditions under which two of the phases are in equilibrium with each other. To describe the system corresponding to a line, it is necessary to specify either the temperature or the pressure; either the temperature or the pressure is changed, then one phase disappears. Thus, the lines represent univariant systems with one degree of freedom,

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*Water is one of the very few substances whose melting point decreases as the pressure is increased; two other common examples are bismuth and type metal. For most substances OC has a steep positive gradient, *i.e.*, an incline towards right.

*e.g.*, water—vapour, water—solid, or solid—vapour system. This also follows from the phase rule :

$$F=C-P+2=1-2+2=1.$$

The triple point O corresponds to the only set of temperature and pressure conditions at which all three phases, solid, liquid, and vapour, are in equilibrium with each other. If either the pressure or the temperature corresponding to this point is changed, one of the three phases will disappear. Thus, the system at O has no degree of freedom; it is invariant. This can be deduced by applying the phase rule : $F=C-P+2=1-3+2=0$.

The various phase equilibria in the one component water system along with their locations in the phase diagram (Fig. 3-6). and degrees of freedom are summarised in Table 3-1.

**Table 3-1**

*Phase equilibria in the water system : Component = 1*

| *Equilibria* | *Location on phase diagram* | *Degree of freedom ($F=C-P+2$)* |
|---|---|---|
| **I. Single Phase equilibria** | | |
| 1. Liquid water | Area AOC, marked water | Two (bivariant)<br>$F=1-1+2$<br>$=2$ |
| 2. Water vapour | Area AOB, marked vapour | |
| 3. Ice | Area BOC, marked ice | |
| **II. Two phase equilibria** | | |
| 1. Water and vapour | Along OA (vaporization curve) | One (univariant)<br>$F=1-2+2$<br>$=1$ |
| 2. Ice and vapour | Along OB (sublimation curve) | |
| 3. Ice and vapour | Along OC (fusion curve) | |
| **III. Three phase equilibrium** | | |
| 1. Ice, water and vapour | At point O (triple point) | Zero (univariant)<br>$F=1-3+2=0$ |

By carefully lowering the temperature water may be cooled below its freezing point (0°C) without solidification occurring. This phenomenon is cooled *supercooling*. It is represented on the phase diagram by the extension of AO to A'. Along the line OA' the liquid-vapour system exists in a condition of *metastable* equilibrium*. On scratching or on adding a small amount of ice to the metastable liquid—vapour system, all of the liquid phase immediately solidifies, that is, changes into the stable solid phase. It may be noted from Fig. 3-6 that at any temperature the metastable system has a higher vapour pressure than the stable system. This indicates the tendency for the metastable system to pass into the stable system.

## 5. Enantiotropy and Monotropy

The existence of the same substance in two or more different crystalline forms is called *polymorphism*. This phenomenon is exhibited by elements and compounds both. The polymorphism of elements is commonly referred to as *allotropy*. Two main types of polymorphism are enantiotropy and monotropy.

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*A metastable equilibrium or state may be defined as one in which the phase which is normally stable under the given conditions does not form unless a small amount of the normally stable phase is already present.

**5-1. Enantiotropy**. The main characteristics of enantiotropy are :

1. Each polymorphic form (allotrope) is stable over a definite range of temperature.

2. At a certain definite temperature, the different solid forms exert the same vapour pressure and can exist in equilibrium with each other. This temperature is called the *transition temperature*.

3. Each polymorphic form can be directly converted into the other by varying the temperature.

The polymorphism of sulphur is one of the best examples of enantiotropy. It exists in two forms : rhombic sulphur and monoclinic sulphur. The transition temperature between the two forms is 95·6°C (under 1 atmosphere pressure). Rhombic sulphur, when heated under 1 atmosphere pressure, changes into monoclinic sulphur at 95·6°C. On the other hand, monoclinic sulphur when cooled under 1 atmosphere pressure, changes into rhombic sulphur at 95·6°C. *The reversible transformation of polymorphic forms into one another at the transition temperature is known as enantiotropy and the polymorphic forms involved are called enantiotropes.*

**5-2. Phase diagram of sulphur**. Since each polymorphic form constitutes a separate phase, sulphur exhibits four phases : liquid sulphur, sulphur vapour, rhombic sulphur, and monoclinic sulphur. However, the sulphur system is a one component system since all the phases are represented by the same chemical substance—sulphur.

The phase diagram of shulphur is shown in Fig. 3-7. AB is the vapour pressure curve of rhombic sulphur and BC is the vapour pressure curve of the monoclinic form. B is the transition temperature (95·6°C) at which each enantiotrope changes into the other if the temperature is varied slowly. If rhombic sulphur is heated strongly, however, the temperature rises rapidly through the transition temperature. The rhombic sulphur retains its form for a while, though in a metastable state, until it melts at 114°C, represented by the point O. The dotted curve BO represents the vapour pressure curve of the metastable rhombic sulphur. A similar situation arises when monoclinic sulphur is cooled below the transition temperature. It does not change into the rhombic form at B but remains in a metastable monoclinic form for a while. This is represented by the dotted line BG. The curve CD is the vapour pressure curve of liquid sulphur; C being the melting point (120°C) of monoclinic sulphur under its own vapour pressure (0·04 mm of mercury).

Curve BE shows the influence of pressure on the transition temperature between the rhombic and monoclinic forms, and curve CE shows the influence of pressure on the melting point of monoclinic sulphur. The metastable curve OF depicts the influence of pressure upon the melting point of rhombic sulphur. It will be noted that the result of applying a high external pressure is to raise the transition temperature as well as the melting points of the monoclinic and rhombic forms. Thus the points B, C, E, and F are all triple points where three phases are in equilibrium with each other as shown in Table 3-2.

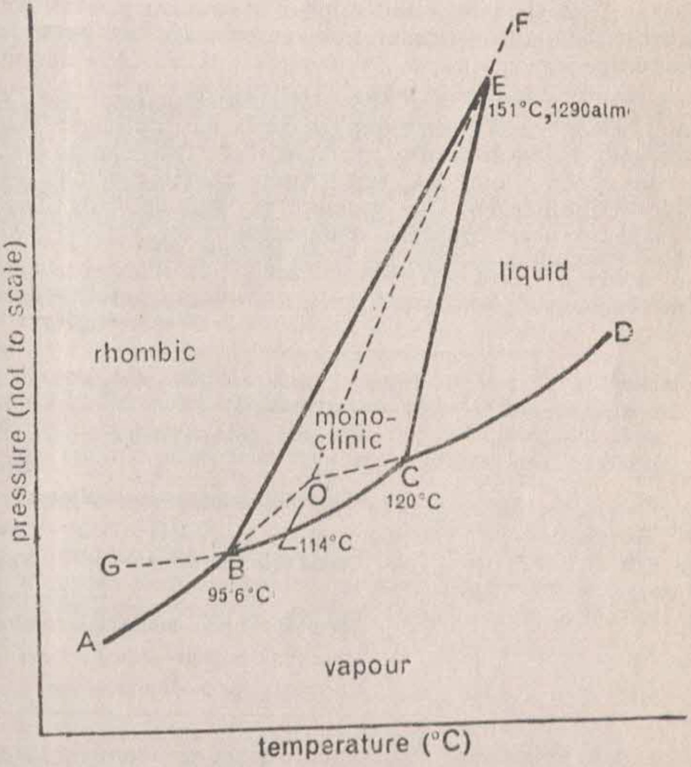

Fig. 3-7. Phase diagram of sulphur.

**Table 3-2.** *Phase equilibria at the triple points in the sulphur system*

| *Triple point* | *Phases in equilibria with each other* |
|---|---|
| B | Rhomic sulphur, monoclinic sulphur, sulphur vapour |
| C | Monoclinic sulphur, liquid sulphur, sulphur vapour |
| E | Rhombic sulphur, monoclinic sulphur, liquid sulphur |
| O | Rhombic sulphur, liquid sulphur, sulphur vapour |

At any triple point, the system has no degrees of freedom, *i.e*, it is invariant. The phase rule also predicts the same : $F=C-P+.$ $2=1-3+2=0$.

The four *areas* marked rhombic, monoclinic, liquid, and vapour represent the various conditions of temperature and pressure under which the corresponding phases are stable. Each area has only one phase, and the phase rule predicts that the number of degrees of freedom is 1—1+2 or 2. This means that both temperature and pressure may be varied independently without the disappearance of the existing phase or the reappearance of a new phase. Thus, the monoclinic sulphur can exist in a stable condition between the limits of temperature and pressure set by the points B and E.

Each curve in the phase diagram represents two phases in equilibrium. Each point along the curve has only one degree of freedom : $1-2+2=1$. For example, if the temperature is specified at any point along BA representing rhombic sulphur—sulphur vapour equilibrium, the pressure is automatically fixed. The various two phase equilibria represented by the various lines in the phase diagram of sulphur are given in table 3-3.

Table 3-3. *Phase equilibria along the curves in the sulphur system*

| *Curve* | *Phases equilibria with each other* |
|---|---|
| 1. AB | Rhombic sulphur—sulphur vapour (*stable*) |
| 2. BO | ,, ,, ,, ,, (*metastable*) |
| 3. BC | Monoclinic sulphur—sulphur vapour (*stable*) |
| 4. BG | ,, ,, ,, ,, (*metastable*) |
| 5. CD | Liquid sulphur—sulphur vapour (*stable*) |
| 6. OC | ,, ,, ,, ,, (*metastable*) |
| 7. BE | Rhombic sulphur—monoclinic sulphur |
| 8. CE | Monoclinic sulphur—liquid sulphur |
| 9. OF | Rhombic sulphur—liquid sulphur (*metastable*) |

5-3. **Monotropy.** The chief features of monotropy are :

1. Only one polymorphic form is stable, any other form being unstable under all conditions.

2. There is no definite temperature at which the two solid forms are in equilibrium with each other.

3. The metastable form can directly change into the stable form; the direct change of the stable form into the metastable form does not occur.

One of the best known examples of monotropy is provided by phosphorus. Its polymorphic form called red phosphorus is stable at all temperatures up to its melting point. The other polymorphic form, called white phosphorus, is the metastable form which changes into the red phosphorus very slowly at room temperature and rapidly on heating. However, red phosphorus cannot be changed directly into white phosphorus. *Such polymorphic forms which cannot reversibly changed into one another are said to be* **monotropic** *and the phenomenon is called* **monotropy**.

**5-4. Phase diagram of phosphorus.** A simplified phase diagram of phosphorus is shown in Fig. 3-8. On this diagram, AB is the vapour pressure—temperature curve for red phosphorus which melts at B corresponding to 590°C. DE is the vapour pressure—temperature curve for white phosphorus which melts at E corresponding to 44°C. At any temperature, the vapour pressure of the metastable white phosphorus is higher than that of the stable red phosphorus. Hence, white phosphorus tends to change into the red form. BC is the vapour pressure—temperature curve for molten red phosphorus. Thus B is the triple point at which solid red phosphorus, liquid red phosphorus, and phosphorus vapour exist in equilibrium with each other. Curves BF and EF depict the effect of pressure on the melting point of white phosphorus and red phosphorus respectively. Thus E is the triple point at which solid white phosphorus, liquid white phosphorus, and phosphorus vapour are in equilibrium.

Curves AB and DE may be extended to meet at F which is theoretically the transition temperature between the two forms of phosphorus. However, the point F has no significance since it is above the melting point of either form at atmospheric pressure.

A stable allotrope does not change spontaneously into the metastable form. Hence, in order to convert red phosphorus into white phosphorus the former is either melted or vaporized and the liquid or vapour obtained cooled rapidly. The system then follows the path CBE and crystals of the white form are deposited at the point E.

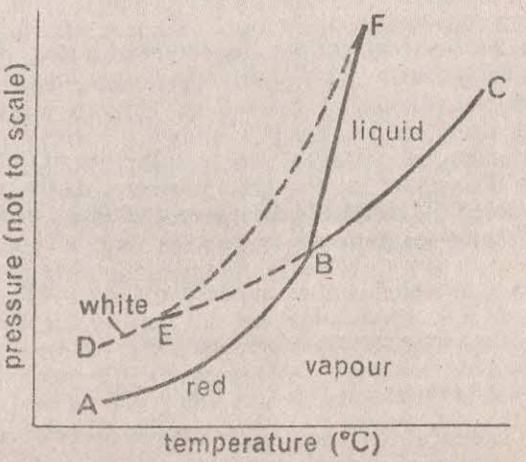

Fig. 3-8. A simplified phase diagram of phosphorus.

## TWO COMPONENT SYSTEMS

## 6. Solutions of Gases in Liquids

When a gas dissolves in a liquid, it may form a physical dispersion, or it may react chemically with the liquid and form new chemical species. Thus, oxygen dissolves in water by means of physical dispersion while ammonia dissolves largely by the chemical reaction : $NH_3+H_2O \rightarrow NH_4^++OH^-$. Carbon dioxide dissolves in water both by physical dispersion and to some extent by chemical reaction with water to form carbonic acid : $CO_2 + H_2O \rightarrow H_2CO_3$. Here, we shall consider the solutions of gases in liquids resulting from physical dispersion.

Gaseous molecules that disperse in a liquid may subsequently escape from the liquid. When the rate of escape equals the rate of dispersal, the system attains the state of equilibrium. In a system consisting of a gas in equilibrium with its saturated solution in a liquid there are two components and two phases, since the solution of the gas in the liquid is itself a single phase That is, C and P are both equal to 2. Applying the phase rule, $F=C-P+2$, the number of degrees of freedom.

$$F=2-2+2=2$$

Thus, for the system to be completely defined the two variables, —temperature and pressure—must be fixed.

**6-1. Influence of pressure : Henry's Law.** The solubility of a gas in a liquid depends upon the pressure of the gas. The quantitative relationship between the pressure of a gas and its solubility is expressed by Henry's Law as follows :

"*At constant temperature the weight of a gas which dissolves in a given volume of a liquid is directly proportional to the pressure of the gas.*"

For example, nitrogen has a solubility of 0·003g in 100g of water at 0°C under atmospheric pressure. If the pressure on the gas is doubled, its solubility increases to 0·006g, or twice as much, under the same temperature condition.

It may be noted that Henry's Law is applicable only when—

(1) the temperature is not very low,

(2) gas pressure is not very high, and

(3) chemical changes either do not occur or are insignificant in the formation of the solution.

Henry's Law can be qualitatively explained both in terms of Le Chatelier's principle and the kinetic theory of gases. According to Le Chatelier's principle, when a system in equilibrium is subjected to a stress, such as a change in temperature or pressure, the equilibrium shifts in the direction that tends to relieve the effect of the stress. Thus when the pressure on a gas in contact with a liquid is increased, more of the gas disperses into the liquid so that the effect of increased pressure is annuled. In terms of the kinetic theory of gases, an increase in pressure leads to a decrease in volume, *i.e.*, a larger number of gas molecules are accommodated in the same space (Fig. 3-9).

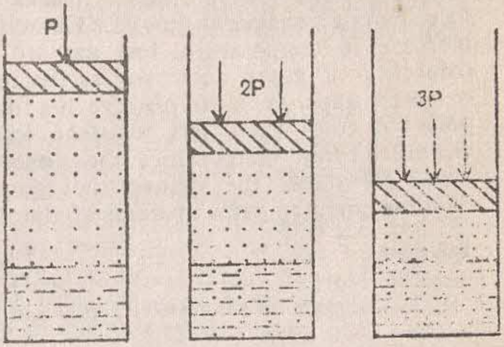

Fig. 3-9. A gas dissolving in a liquid under pressure (dots represent molecules of the gas.)

Since according to Boyle's Law the volume of a given mass of gas is inversely proportional to the pressure, Henry's Law may also be stated in the form : "*The volume of a gas which dissolves in a given volume of a liquid at constant temperature is independent of pressure.*"

*Applications of Henry's Law.* The production of carbonated beverages depends on Henry's Law. The gas which adds the acidic flavour to soft drinks is carbon dioxide. Under ordinary atmospheric pressure the amount of gas which dissolves is not enough to create the desired acidity. Hence, carbon dioxide is forced into the liquid beverage under a pressure of 5 to 10 atmospheres, causing enough carbon dioxide to dissolve to give the proper bite to the drink. The bottle is tightly capped to prevent escape of carbon dioxide and maintain the pressure. When the cap is removed, the pressure is reduced to one atmosphere, and much of the carbon dioxide escapes from solution as gas bubbles. This is why carbonated beverages *fizz* or *effervesce* when poured into an open glass tumbler often producing abundant foam.

In the Bosch process for the manufacture of hydrogen, carbon dioxide is removed from its mixture with hydrogen by forcing it into water under 50 atmospheres pressure. Henry's law is also applied in storing acetylene by dissolving it in acetone under a pressure of about 30 atmospheres.

**6-2. Influence of temperature.** In a gas the molecules are far apart and they interact very weakly. When a gas dissolves in a liquid, the gas molecules come close to the solvent molecules and they attract each other, lowering the potential energy. Hence, when a gas dissolves in a liquid, *heat is evolved*. It follows, therefore, from a consideration of Le Chatelier's principle, that with an increase in temperature, less gas will dissolve. In general, the solubility of gases decreases as the temperature is raised. It is a common experience to observe the formation of gas bubbles in a glass of cold water left to stand in a warm room; as the water warms to room temperature the dissolved air escapes as bubbles. Table 3-4 shows the influence of temperature upon the solubility of some common gases in water at atmospheric pressure.

**Table 3-4.** *Temperature and solubility of gases*

| *Gas* | *Amount of gas dissolving in 100g of water at 1 atm pressure*<br>*0°C* | *20°C* | *60°C* |
|---|---|---|---|
| Oxygen | 0·007g | 0·004g | 0·002g |
| Nitrogen | 0·003g | 0·002g | 0·001g |
| Carbon dioxide | 0·337g | 0·200g | 0 070g |
| Ammonia | 0·983g | 0·574g | 0·225g |

If a solution of ammonia in water is boiled for some time in the open air, the dissolved gas is completely expelled leaving behind pure water. This ready removal of a gas from a boiling solution occurs because the gas diffuses into the bubbles of vapour which are removed more rapidly than the liquid is itself vaporized. It is, therefore, wrong to infer that the solubility of a gas in water at 100°C is nil, because the gas is not in equilibrium with the solution when the solution is boiled in open air. If the ammonia solution is boiled in such a way that the boiling solution remains in contact with the expelled gas at 1 atmosphere pressure, the concentration of ammonia in solution would remain at 0·15g in 100g of water which is the equilibrium level for this temperature, however, long the boiling is continued. Ammonia in water may also be removed by bubbling air through the solution because the continual flow of air sweeps the volatile ammonia and prevents the establishment of equilibrium. These examples show why the solutions of gases in liquids should be regarded in terms of an equilibrium between two phases.

## 7. Solutions of Liquids in Liquids

Depending upon their relative solubilities in one another, two liquids may be—

(*i*) *completely miscible* in one another,

(*ii*) *partially miscible* in one another, or

(*iii*) *immiscible* in one another.

**7-1. Completely miscible liquid pairs.** Two liquids are said to be completely miscible when they dissolve in each other in all proportions to give a homogeneous mixture, *e.g.*, alcohol and water, benzene and toluene, etc. If the vapour pressure above a mixture of two miscible liquids is plotted against the composition of the mixture, it is found that such mixtures, are of three different types.

**Type 1**. *Whatever the composition, the vapour pressure always lies between the vapour pressure of the two pure liquids.* In such a case, the plot of the partial pressure of each pure liquid against the composition of the liquid mixture will be a straight line passing through the origin as indicated by curves *QR* and *PS* (Fig. 3-10). The total vapour pressure, that is, the sum of the partial pressures, will, therefore, also be a straight line as indicated by *PR*. Solutions behaving thus are said to be *ideal solutions*. Benzene—toluene solution is an example of ideal solution.

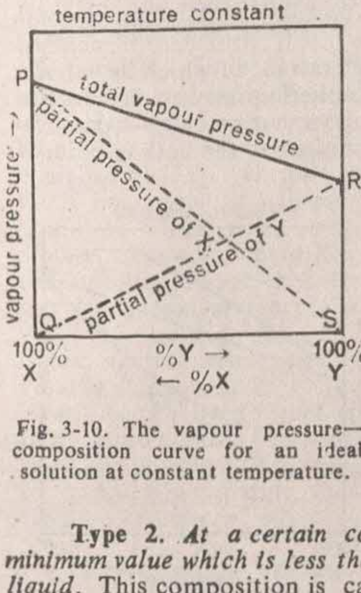

Fig. 3-10. The vapour pressure—composition curve for an ideal solution at constant temperature.

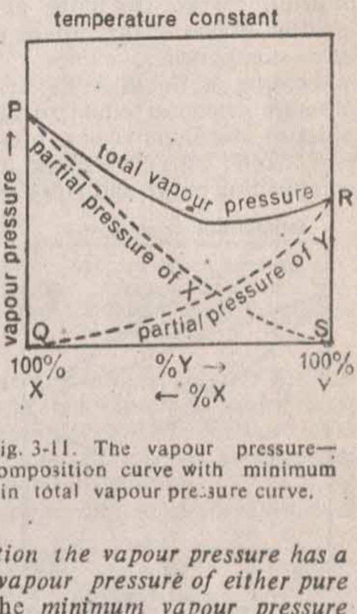

Fig. 3-11. The vapour pressure—composition curve with minimum in total vapour pressure curve.

**Type 2.** *At a certain composition the vapour pressure has a minimum value which is less than the vapour pressure of either pure liquid*. This composition is called the *minimum vapour pressure composition.* In the vapour pressure—composition curve for such a solution the total vapour pressure curve passes through a minimum value below the vapour pressures of the component liquids (Fig. 3-11). Nitric acid-water, and hydrochloric acid—water solutions are examples of this type of solutions.

**Type 3.** *At a certain composition the vapour pressure has a maximum value which is greater than the vapour pressure of either pure liquid*. The composition is called the *maximum vapour pressure composition.* In the vapour pressure-composition curve for such a solution the total vapour pressure curve passes through a maximum value above the vapour pressures of the component liquids (Fig. 3-12.) Ethylalcohol—water, and acetone—methyl alcohol solutions are examples of this type of solutions.

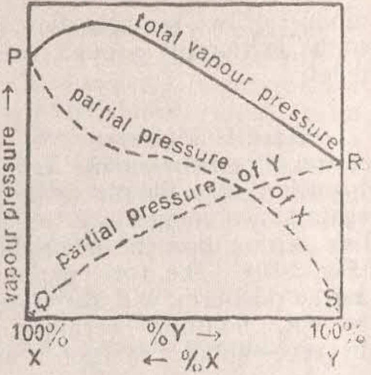

Fig. 3-12. The vapour pressure—composition curve with maximum in total vapour pressure curve.

The liquid—liquid solutions that have vapour pressures smaller or greater than the vapour pressure of either component are called *non-ideal solutions*. The vapour pressure—composition curves of the three types of solutions are shown all together in Fig. 3-13. The boiling point—composition curves of the three types of solutions are shown in Fig. 3-14. It may be noted that the boiling point—composition curves are more or less inverted shapes of the vapour pressure—composition curves. This is because a liquid boils at a temperature at which its vapour pressure becomes equal to the atmospheric pressure. Hence, the point of maximum vapour pressure in a vapour pressure—composition curve will correspond to a minimum in the boiling point—composition curve and *vice-versa*.

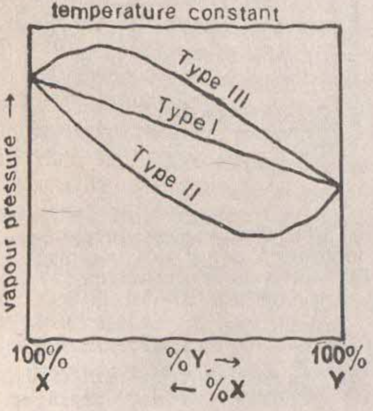

Fig. 3-13. Vapour pressure—composition curves of the three types of solutions.

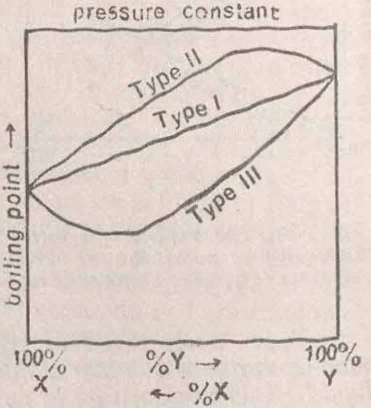

Fig. 3-14. Boiling point—composition curves of the three types of solutions.

## 8. Fractional Distillation

*Fractional distillation is the process of separation of a mixture of liquids which have different boiling points, by collecting separately 'fractions' boiling at different temperatures.* It is possible only when the vapour from the liquid mixture has a composition different from that of the boiling liquid mixture itself. Hence, to understand the process of fractional distillation it is essential to have an idea of the composition of the vapour phase and that of the liquid phase in equilibrium with it at different boiling temperatures. For this purpose the composition of the liquid and its vapour present in equlibrium with it are plotted against the boiling point of the liquid mixture when two separate curves are obtained for each type of solutions (Fig, 3-15, 3-18, and 3-19).

**8-1. Fractional distillation of Type I liquid mixtures** (*Ideal solutions*). The temperature—liquid/vapour composition diagram of a Type I liquid mixture is shown at Fig. 13-15. The upper curve represents the composition of the vapour while the lower curve represents the composition of the liquid. At any particular composition of liquid the vapour over it is always richer in the more volatile (*i.e.*, low boiling) component than is the liquid with which it is in equlibrium. Thus, when at temperature T a liquid of composition $L_1$ commences to boil it gives rise to vapour of composition, $V_1$. If the vapour $V_1$ is condensed it will produce liquid $L_2$ which is richer in the more volatile component X. The residual liquid is richer in the less volatile component Y so that the boiling point of the liquid mixture rises steadily towards the boiling point of the less volatile component Y. If liquid $L_2$ is heated vapour of composition $V_2$ will be produced which will condense to liquid $L_3$ further richer in the more volatile component X. Thus, by a series of vaporizations and condensations, called fractional distillation, it is possible to completely separate the two components of an ideal solution from one another.

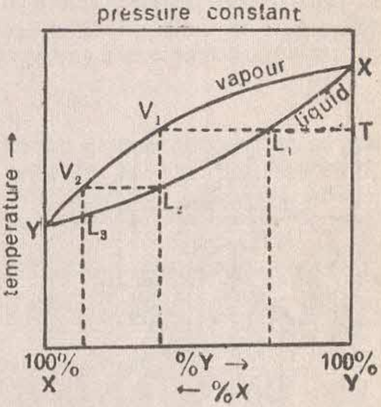

Fig. 3-15. Temperature—liquid/vapour composition curve of Type I liquid mixtures (ideal solutions).

**Fractionating columns.** In actual practice the successive vaporizations and condensations are effected in one and the same operation by means of a fractionating column. The fractionating column consists of a long column with specially designed bulbous surfaces (Fig. 3-16). It is fitted into the mouth of the distillation flask (Fig. 3-17) in which the liquid mixture to be fractionated is heated. The vapour from the flask passes upward the fractionating column and is progressively condensed. Thus, the ascending vapour and descending liquid are brought into as intimate contact as possible so that an equlibrium between the two exists at every stage. The ascending vapour progressively loses the less volatile component by condensation as it is cooled by the descending liquid. The descending liquid, on the other hand, progressively loses the more volatile component as it is heated by the ascending vapour. The effect is the same as repeated condensation and vaporization and, under ideal conditions, the vapour of the more volatile component issues from the top of the column (Fig. 3-17). Fractional distillation is of great importance in the separation of oxygen, nitrogen, and inert gases from liquid air, and in the refining of petroleum. Industrial fractionating columns are extremely complicated structures and may be up to 30 metres tall.

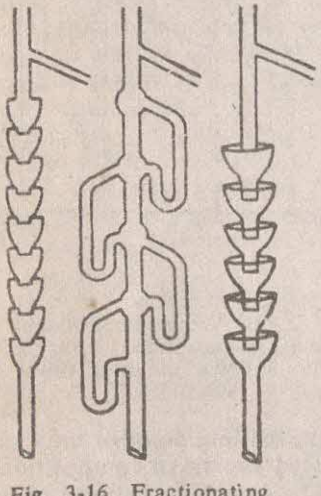

Fig. 3-16. Fractionating columns.

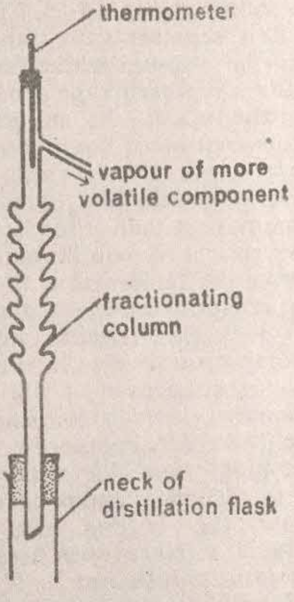

Fig. 3-17. Fractional distillation.

**8-2. Fractional distillation of Type II liquid mixtures** (*maximum boiling point mixtures*). In the case of liquid—liquid solutions where the total vapour pressure curve exhibits a minimum (Fig. 3-10), it is impossible to separate the components by distillations. The temperature—liquid/vapour composition diagram of a Type II liquid mixture is shown at Fig. 3-18. On distillation, the composition of the residual liquid mixture changes gradually and its boiling point rises slowly until the liquid remaining in the flask has the composition C. Now the vapour has the same composition as the liquid with which it is in equilibrium and hence the two distil together at constant temperature. Such mixtures which distil over unchanged are known as *azeotropic mixtures* or simply *azeotropes*. Thus, in the case of Type II solutions complete separation of components cannot be achieved by distillation. Instead, only that constituent which is present in greater proportion than in the azeotropic mixture can be obtained pure.

Suppose the liquid—liquid solution of Type II has the composition $L_1$ (greater proportion of the more volatile component X). When heated, it commences to boil at the temperature T evolving vapour of composition $V_1$. If the vapour at $V_1$ is condensed to a liquid, its composition would correspond to $L_2$. When heated this liquid evolves vapour of composition $V_2$. Thus, the vapour becomes progressively richer in X until finally the pure component X distils off The residual liquid becomes progressively poorer in X until it attains the composition of the constant boiling-point mixture C which distils off unchanged at a constant temperature, $T_c$.

The liquid—liquid solution with a greater proportion of the volatile component Y will give pure Y as the first fraction. Suppose, the composition of the mixture corresponds to $L_4$. On heating it gives rise to vapour $V_4$ which condenses to give liquid $L_5$, with a still greater proportion of Y. When heated, $L_5$ evolves vapour $V_5$ and so on until pure Y distils off. With the loss of Y the residual liquid becomes progressively richer in X and when it attains the composition of the point C the azeotropic mixture distils over unchanged at a constant temperature, $T_c$.

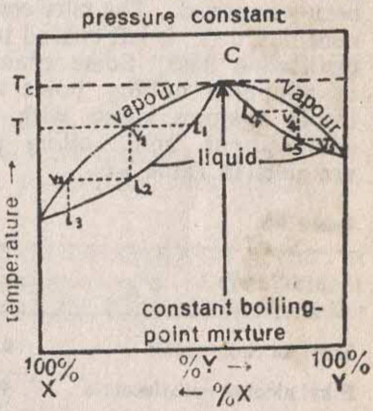

Fig. 3-18. Temperature—liquid/vapour composition curve of Type II liquid mixtures.

There are several liquid—liquid solutions which form maximum boiling point mixtures. Some of such mixtures along with their compositions and boiling points are given in Table 3-5.

**Table 3-5** *Some maximum boiling-point mixtures*

| *Mixture* | *Composition* | *Boiling point* |
|---|---|---|
| Sulphuric acid—water | 98·7 per cent $H_2SO_4$ | 338·0°C |
| Nitric acid—water | 68·0 per cent $HNO_3$ | 125·5°C |
| Hydrochloric acid—water | 20·2 per cent HCl | 108·6°C |
| Hydrobromic acid—water | 48·0 per cent HBr | 125·0°C |

**8-3. Fractional distillation of Type III liquid mixtures** ***(minimum boiling point mixtures).*** In the case of Type III liquid mixtures, too, pure components cannot be separated by distillation. The temperature—liquid/vapour composition curve of such a mixture is shown at Fig. 3·19. Suppose the composition of the liquid is $L_1$. When heated, it evolves vapour of composition $V_1$ which cools to give liquid $L_2$. On heating $L_2$ give rise to vapour $V_2$ and so on. Finally, the liquid attains the composition of the minimum constant boiling point mixture C and this continues to distil over until whole of X has been vaporized. The pure component liquid Y is left behind in the distillation flask. Some examples of minimum boiling point azeotropic mixtures along with their compositions and boiling point are given in Table 3-6.

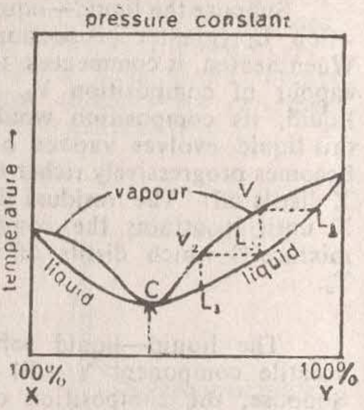

Fig. 3-19. Temperature—liquid/vapour composition curve of type III mixtures (point C corresponds to the temperature at which constant boiling point mixture distils).

**Table 3-6.** *Some minimum boiling point mixtures*

| *Mixture* | *Composition* | *Boiling point* |
|---|---|---|
| Ethyl alcohol—water | 95·6 per cent $C_2H_5OH$ | 78·13°C |
| Ethyl alcohol—ethylacetate | 46·4 per cent $C_2H_5OH$ | 71·80°C |
| Ethyl acetate—water | 30·5 per cent water | 70·40°C |
| Pyridine—water | 59·0 per cent pyridine | 92·00°C |

## 9. Partially Miscible Liquids

Some liquids exhibit *partial* miscibility in one another. That is, they dissolve in each other only in certain proportions and not in all proportions. For example, if phenol is added to water drop by drop, at first it dissolves completely forming a homogeneous solution, but there comes a point when phenol no further dissolves and two separate liquid layers are formed. The upper layer is a saturated solution of phenol in water and the lower one is a saturated solution of water in phenol. If more phenol is added a stage is ultimately reached when whole of the water present dissolves in phenol, and the boundary between the two layers then disappears. Diethyl ether—water, aniline—water, nicotine—water, etc , are some more examples of partially miscible liquid pairs.

If the compositions of the conjugate solutions of the phenol-water system are plotted against temperature, a diagram shown at Fig. 3-20 is obtained. In this diagram, at any temperature $t_1$ the points A and B give the compositions of the two layers in equilibrium with each other. As the temperature is raised the compositions of the two conjugate solutions approach one another due to increased solubility of each liquid in the other. At point C, corresponding to 65·8°C at atmospheric pressure, the two layers merge into one, *i.e.*, become identical in composition. This lowest temperature at which the two liquids are miscible in all proportions is known as the *critical solution temperature**. The shaded area ACB in the diagram corresponds to conditions of immiscibility, and is called the *miscibility gap*. At all points outside the miscibility gap the two components phenol and water are completely miscible in one another.

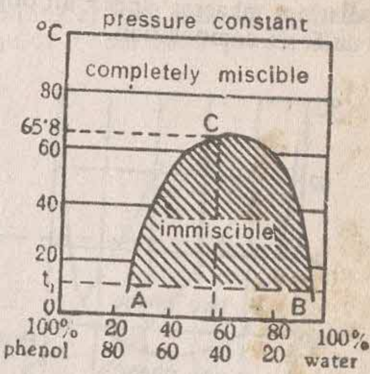

Fig. 3-20. Miscibility of phenol and water.

The phenol-water system outside the curve ACB consists of one liquid phase only; if the vapour phase is neglected. The number of components in the system is two. So, by the Phase Rule the number of degrees of freedom.

$$\begin{aligned} F &= C-P+2 \\ &= 2-1+2 \\ &= 3 \end{aligned}$$

However, the pressure variable is taken as fixed at one atmosphere. Hence, the number of degrees of freedom will be 2. These are temperature and pressure and both must be stated to define completely a system consisting of only one phase.

In certain pairs of partially miscible liquids, *e.g.*, triethylamine and water, the mutual solubility increases on lowering the temperature. Such pairs are completely miscible below a certain temperature and are immiscible in certain proportions above it. The miscibility curves in such case are reversed (Fig. 3-20).

The system nicotine—water has an upper critical solution temperature like the phenol—water system and a lower critical solution temperature like the triethylamine—water system. Thus, under high pressures its miscibility curve is a closed loop as shown in Fig. 3-22. At the conditions corresponding to the area inside the closed loop the two liquids are immiscible and exist as two distinct phases; under all other conditions they from a solution of uniform composition.

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*Experiments show that the critical solution temperature is very sensitive to the presence of impurities, falling to room temperature on adding about 1 per cent of soap and rising several degrees if even trace of benzene are introduced,

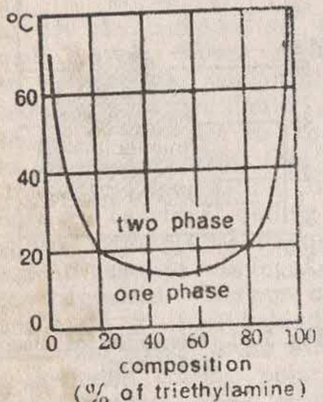


Fig. 3-21. Miscibility of triethylamine and water.

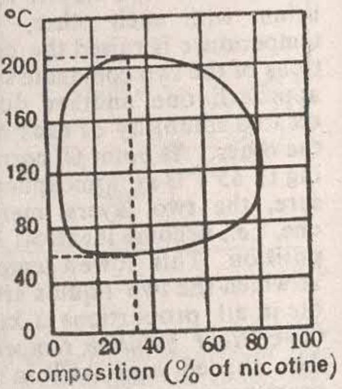


Fig. 3-22. Miscibility of nicotine and water.

## 10. Immiscible Liquids

Many pairs of liquids are completely immiscible. Whe placed together in the same vessel in any proportions they separate out into two quite distinct layers. Examples are carbon disulphide and water, carbon tetrachloride and water, and mercury and water. In a mixture of two completely immiscible liquids A and B, each liquid exerts its own characteristic vapour pressure independently of the other. Hence, the total vapour pressure, $P_{TOTAL}$, above the mixture will be equal to the sum of the vapour pressures of pure A and pure B at that temperature. That is,

$$P_{TOTAL}=P_A+P_B \text{ (at T)}$$

where $P_A$ is the vapour pressure of pure A and $P_B$ the vapour pressure of pure B at that temperature.

On heating the mixture, its total vapour rises with temperature until it is equal to the atmospheric pressure when the system boils. At this temperature, *i.e.*, at the boiling point of the mixture,

$$P_A+P_B=\text{atmospheric pressure}$$

Since the vapour pressure of any single liquid at this temperature is less than the atmospheric pressure, the mixture will boil at a temperature which is lower than that at which either pure liquid boils (Fig. 3-23). Further, since there are two components and three phases (liquid A, liquid B, and the vapour of A and B), the system is univariant. Thus, at a given temperature there can be no change in the total vapour pressure or in composition. Alternately, if pressure is constant (let it be atmospheric pressure), the boiling point as well as the composition of the vapour (and hence of the distillate) will remain unchanged. That is, the mixture will distil at a constant temperature so long at least some of each component is present giving the two liquids in constant proportion in the distillate.

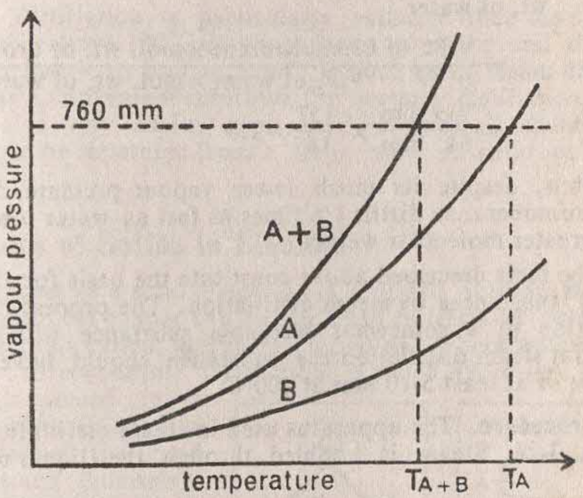


Fig. 3-23. Principle of steam distillation.

Now, since at a given temperature gases exert pressures in proportion to the concentration of the molecules, it follows that the ratio of vapour pressures of A and B ($P_A$ and $P_B$) at the boiling point of the mixture is the numerical ratio between the number of moles of A and B distilling from the mixture. That is,

$$\frac{N_A}{N_B}=\frac{P_A}{P_B}$$

where $N_A$ and $N_B$ are the moles of A and B in the vapour.

If $W_A$ and $W_B$ be the actual weights of A and B in the vapour and $M_A$ and $M_B$ their respective molecular weights, $N_A=W_A/M_A$ and $N_B=W_B/M_B$. Substituting these values in the above equation,

$$\frac{W_A}{M_A}\Big/\frac{W_B}{M_B}=\frac{P_A}{P_B}$$

Or,
$$\frac{W_A}{W_B}=\frac{P_A\,M_A}{P_B\,M_B}$$

The foregoing equation tells that in the distillation of a mixture of two immiscible liquids, the relative weights of the two liquids in the distillate are directly proportional both (1) to the vapour pressures of the liquids at the distillation temperature and

(2) to their molecular weights. This may be illustrated by considering the distillation of a mixture of water and bromobenzene ($C_6H_5Br$), a liquid completely immiscible with water. The mixture bals at 95·3°C, at which temperature the vapour pressure of water is 641 mm. The vapour pressure of bromobenzene at 95·3°C will, therefore, be 760 mm−641 mm=119 mm. Hence, the ratio of bromobenzene to water in the distillate will be as follows :

$$\frac{\text{wt. of bromobenzene}}{\text{wt. of water}}$$

$$=\frac{\text{V.P. of bromobenzene} \times \text{mol. wt. of bromobenzene}}{\text{V.P. of water} \times \text{mol. wt. of water}}$$

$$=\frac{119 \text{ mm}}{641 \text{ mm}} \times \frac{157}{18}=1.6$$

Thus, despite its much lower vapour pressure, on a weight basis bromobenzene distils 1·6 times as fast as water owing to its much greater molecular weight.

The facts described above constitute the basis for the separation of substances by steam distillation. The process involves the distillation of a somewhat insoluble substance with water. For successful steam distillation the substance should have a vapour pressure of at least 5-10 mm at 100°C.

**Procedure.** The apparatus used in steam distillation is shown in Fig. 3-24. Steam is bubbled through the liquid mixture in a

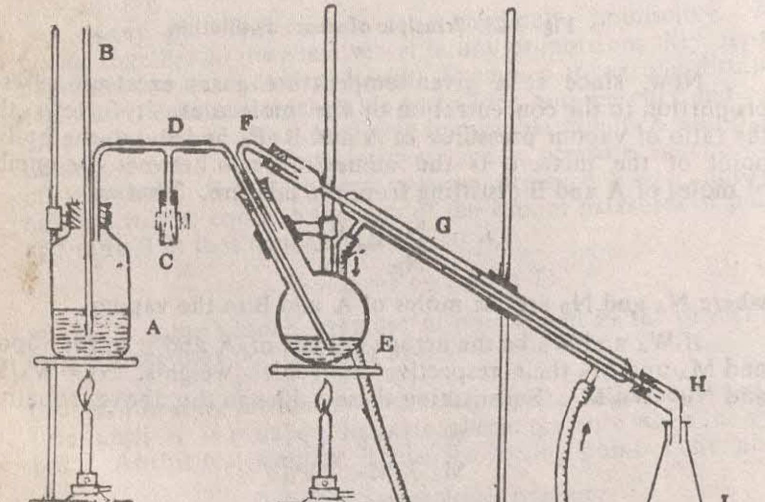


Fig. 3-24. Assembly for steam distillation.

[A. Steam generating can, B. Safety tube, C. Pinch cock, D. Delivery tube, E, Flask containing the mixture, F. Tube connecting steam distillation flask to Liebig's condenser G. Liebig's condenser, H. Adaptor, I. Product of steam distillation] flask. The steam condenses giving up its latent heat of vaporization and eventually causing the mixture to boil. The vapour of the immiscible organic substance and steam escape from the mixture. These are condensed in a descending condenser and collected in a receiver. If the substance is a liquid, it is seperated from the water by using a separating funnel; if a solid, by filtration. Solid and non-volatile impurities are left behind in the distillation flask.

Steam distillation is particularly valuable when the desired substance boils above 100°C at atmospheric pressure and decomposes at or below its boiling point. In such cases, steam distillation serves as a convenient substitute for vacuum distillation. The process is also very useful when a relatively small amount of a substance is to be separated from a large bulk of solid or tarry material.

## 11. Solutions of Solids in Liquids

The process of a solid dissolving in a liquid solvent without any severe chemical change can be explained in terms of solvent—solute interactions called, in general, *solvation*. Where water is the solvent, the solvent-solute interaction is called *hydration*. When a crystal is placed in a liquid in which it is soluble, the molecules of the liquid begin to attach themselves to the constituent particles of the lattice (solvation). For example, polar water molecules (Fig. 3-25) attach themselves to the Na+ and Cl− ions in sodium chloride crystal with their oppositely charged ends directed towards the ions. On the other hand, water molecules attach themselves to sugar molecules by hydrogen bonding through the hydroxyl groups of the latter.

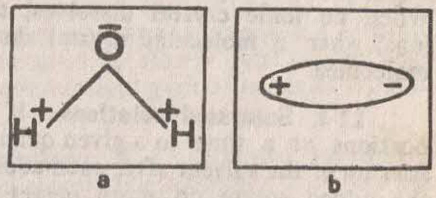
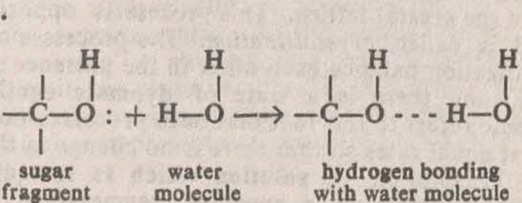


**Fig. 3-25. Polar water molecule represented as in (a), and for simplicity, as in (b).**



$$-\underset{|}{\overset{|}{C}}-\overset{H}{\overset{|}{\ddot{O}}}: + H-\overset{H}{\overset{|}{O}} \longrightarrow -\underset{|}{\overset{|}{C}}-\overset{H}{\overset{|}{O}}\cdots H-\overset{H}{\overset{|}{O}}$$

The solvent-solute interactions are accompanied with the release of energy called *energy of solvation* (*energy of hydration*, if the solvent is water) which causes the affected crystal particles to vibrate vigorously. Provided the energy of solvation exceeds the energy needed to disrupt the lattice (*i.e.*, lattice energy), the solvated particles break away from the solid crystal into the solvent, and further particles become solvated. The process continues causing the solid to 'dissolve' in the liquid. This is shown diagrammatically in Fig. 3-26. The dissolution in ionic lattices is further aided in a highly polar solvent, *e.g.*, water, as the attraction between the ions is greatly reduced by the high dielectric constant of the solvent.*

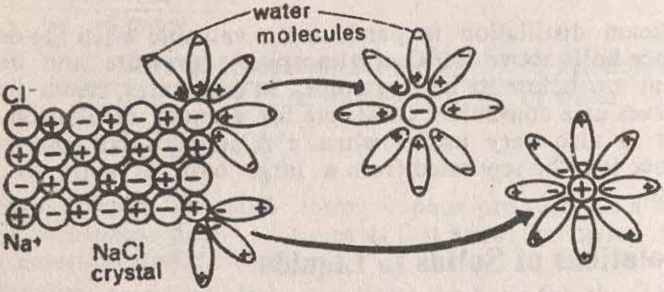


Fig. 3-26. NaCl dissolving in water.

As a general rule, polar substances are soluble in polar solvents and non-polar substances are soluble in non-polar solvents. When an ionic crystal dissolves, the resulting solution contains ions; when a molecular crystal dissolves, the solution contains molecules.

**11-1. Saturated solutions.** If a solute is added in small portions at a time to a given quantity of a solvent, with vigorous stirring of the solvent after each addition, a stage is reached when the added solute no more passes into solution and remains undissolved. At this stage, it appears that the dissolving process stops. Actually, the particles of the solute continue to leave the crystalline solid as a result of solute—solvent interaction and go into solution. However, as the particles of solute in solution move about by diffusion, some of them collide with the solid and take up positions in the crystal lattice. This process is opposite of dissolution and is called *crystallization*. The processes of dissolution and crystallization balance each other in the presence of undissolved solute, and there is a state of **dynamic equilibrium**. The term dynamic refers to the fact that both processes occur continuously but at equal rates so that there is no change in the amount of the solute in solution. **A solution which is in equilibrium with the undissolved solute at a specified temperature is called a saturated solution.** That there occurs a continual exchange of particles of solute between the solid and solution can be shown by mixing some solid containing a radioactive isotope with a saturated solution, when the latter soon becomes radioactive by exchange. Similarly, if a crystal of imperfect shape is placed in a saturated solution of the same crystalline solid, it slowly 'mends' its shape by loss of particles to the solution and gain of particles from the solution (Fig. 3-28).

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*The attractive force between two opposite charges $Q_1$ and $Q_2$ at a distance $d$ is given by $\frac{Q_1.Q_2}{E.d^2}$, where E is the dielectric constant of the medium between the charges. The dielectric constant is a measure of the tendency of the molecules to orient themselves in an electric field and depends on the dipole moment of individual molecules. For water E is about 80, so in its presence the binding forces between the ions will be reduced to an eightieth of their original value.

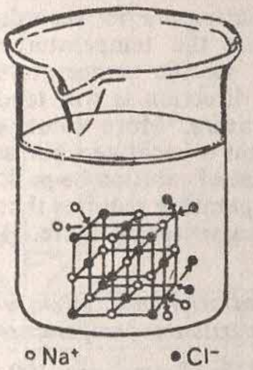


**Fig. 3-27. In a staturated solution of a salt containing undissolved salt, the ions move from the crystal lattice into solution and back into the crystal lattice pattern.**

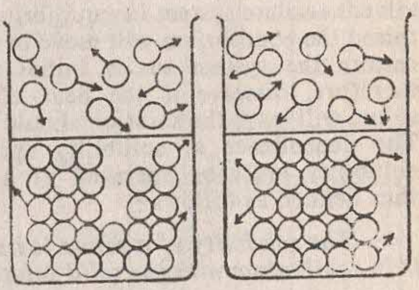


**Fig. 3-28. An imperfect crystal mends its shape when placed sufficiently long in a saturated solution (left) by simultaneous dissolution and crystallization (right).**

**11-2. Supersaturated solutions**. If a saturated solution of a solid solute is prepared at an elevated temperature and then permitted to cool, the excess solute usually separates from the solution by crystallization. However, if the hot saturated solution is allowed to cool undisturbed after removing the undissolved solute, crystallization often does not take place. The solution then contains more solute than can be held in equilibrium with the undissolved solute. This state is called *supersaturation* and the solution is said to be **supersaturated**. If the supersaturated solution is agitated by stirring or shaking, or a 'seed' crystal of the solute is introduced into it, the crystallization of the excess solute occurs; after crystallization a saturated solution remains. Thus, a supersaturated solution represents a system in a metastable (unstable) condition.

**11-3. Effect of temperature on the solubility of solids.** The process of dissolution of a solid is always accompanied with either the evolution or the absorption of heat. The reverse processes of dissolution and crystallization under conditions of equilibrium between a solid and its saturated solution may be represented as follows :

(1) solute + solvent + *heat* $\rightleftharpoons$ solution (*negative heat of solution*)

(2) solute + solvent $\rightleftharpoons$ solution + *heat* (*positive heat of solution*)

In the case of solutes which absorb heat on dissolving (*i.e.*, with a negative heat of solution), the solubility increases with a rise in temperature; the reverse holds for solutes with a positive heat of solution. These effects of temperature variation are in accordance with Le Chatelier's Principle. Thus, when the temperature of a solvent—solute system in equilibrium at a specific temperature is raised the equilibrium will move in such a direction as will tend to restore the system to its initial temperature. More solute will, therefore, dissolve if the heat of solution is negative while some solute will leave the solution should the heat of solution be positive. The dependence of solubility upon temperature requires that the solubility must be specified at a particular temperature. It is thus defined as follows :

*The solubility of a solute is its concentration in solution, which is in equilibrium with the solid solute at a particular temperature.*

The solubility is usually expressed in grams per 100 g of solvent at a specified temperature. Each substance has a characteristic solubility in a given solvent. For example, a saturated solution of copper sulphate in water at 0°C contains 14·3 g of it in 100g of watet. The solubility of copper sulphate in water is, therefore, 14·3g per 100g of water at 0°C.

**11-4. Determination of solubility.** The solubility of a solid at a given temperature is determined in the following steps :

1. A saturated solution of the substance is prepared at the given temperature.

2. Some quantity of the saturated solution is transferred into a weighed dish which is weighed again (difference in the two weights is the weight of the solution in the dish), and evaporated to dryness.

3. The dish with the solid residue is weighed (this weight minus the weight of the dish is the weight of the residue).

The solubility is calculated from the weight of the saturated solution taken and the weight of the residue obtained from it.

**11-5. Solubility curves.** The graphical representation of the relationship of solubility and temperature for a solid is called its solubility curve. The solubility curves for a few common solids are shown in Fig. 3-29.

Following points are noteworthy in connection with solubility curves :

1. With a few exceptions (*e.g.*, ceric sulphate, $Ce_2(SO_4)_3$, and anhydrous sodium sulphate), the solubility of solids increases with rise in temperature. The effect of temperature on the solubility of some solids, *e.g.*, potassium nitrate, lead nitrate, etc. is much more marked than in others The solubility of sodium chloride changes only very slightly with a rise in temperature.

(2) The shape of the curve shows the rate of change of solubility with temperature. A steep curve shows a rapid change; a flat curve shows a slow change.

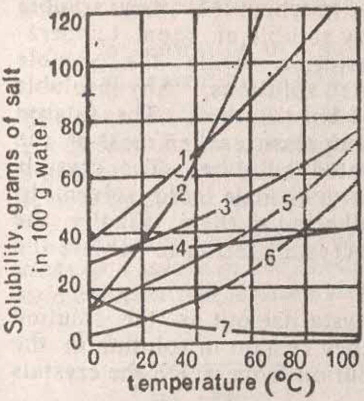


Fig. 3-29. Solubility curves of—
(1) $Pb(NO_3)_2$, (2) $KNO_3$. (3) $NH_4Cl$
(4) NaCl, (5) $CuSO_4$, (6) $KClO_3$,
(7) $Ce_2(SO_4)_3$.

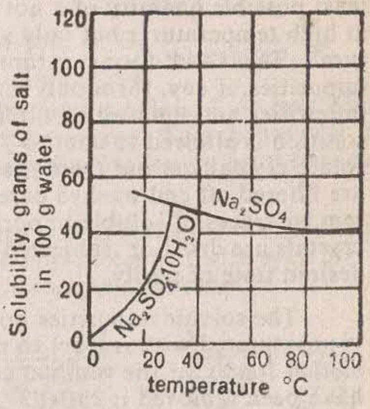


Fig. 3-30. Solubility curve of sodium sulphate.

(3) A sharp break in a solubility curve indicates the formation of a compound with a different degree of hydration whose solubility is different from that of the original substance. For example, the solubility curve of sodium sulphate (Fig. 3-30) has a sharp break at 32·5°C at which temperature $Na_2SO_4.10H_2O$ loses its water of hydration and changes to the anhydrous salt, $Na_2SO_4$. The curve up to 32·5° represents the effect of rising temperature on the solubility of $Na_2SO_4.10H_2O$ and the curve beyond it represents the effect of rising temperature upon the solubility of $Na_2SO_4$.

**11-6. Rate of Solution.** Rate of solution, *i.e.*, the amount of solute passing into the solution per unit of time depends upon the following factors :

1. *Nature of solute.* More soluble substances dissolve more rapidly than the less soluble ones.

2. *State of division.* The dissolution of a solid is the result of the interaction of its particles at the surface with the solvent molecules. Hence, the more finely divided the solute (which means greater surface area per unit mass), the greater will be its rate of solution.

3. *Agitation of mixture.* Stirring or shaking the solvent—solute mixture increases the contact between the solvent and the solute, and thus increases the rate of solution.

4. *Heating.* Heating not only increases the solubility of most solids, it also results in convection currents which cause agitation of the mixture.

**11-7. Recrystallization.** This is the most important method employed in industry and in the laboratory for the purification of organic and inorganic solids. The crude solid is dissolved in the least possible quantity of a hot solvent in which it is very soluble at high temperatures but only sparingly soluble at room temperature. The solid forms saturated solution while the soluble impurities, if any, form only unsaturated solutions. Any insoluble impurities are removed by filtering the hot solution. The filtered solution is allowed to cool to room temperature when most of the solute crystallizes out from the saturated solution. The crystals are filtered off and washed carefully with a little cold solvent to remove traces of soluble impurities adhering to them. Finally the crystals are dried or subjected to recrystallization to achieve the desired state of purity.

The soluble impurities do not crystallize out as the solution is unsaturated with respect to them; they remain in solution in the *mother liquor*, as the residual cold solution from which the crystals have been removed is called.

**11-8. Fractional crystallization.** Two substances A and B having similarly shaped solubility curves (Fig. 3-31) and present in comparable proportions in a mixture can be separated by fractional crystallization. A solution of the mixture is prepared and concentrated gradually by boiling or by evaporation. Crystals of the less soluble compound A are first deposited mixed with some of B. These crystals are removed as the first crop or *fraction*. The mother liquor is now concentrated when crystals of A and B in about equal proportion are deposited, and these are also removed. The mother liquor is now further concentrated when a third fraction consisting mostly of crystals of B mixed with some of A is obtained. Each of these fractions is now separately subjected to the same process using fresh solvent. After repeated fractional crystallizations pure samples of A and B are obtained.

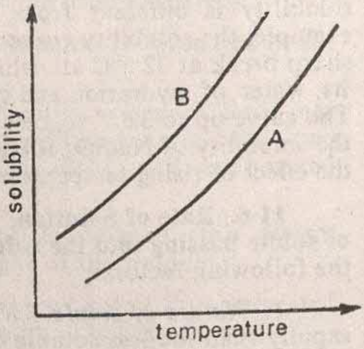


Fig. 3-31. Solubility curves of A and B.

The common solvents employed for recrystallization and fractional crystallization are water, alcohol or methylated spirit, ether, glacial acetic acid, acetone, petrol, and benzene. Sometimes a mixture of two solvents is used.

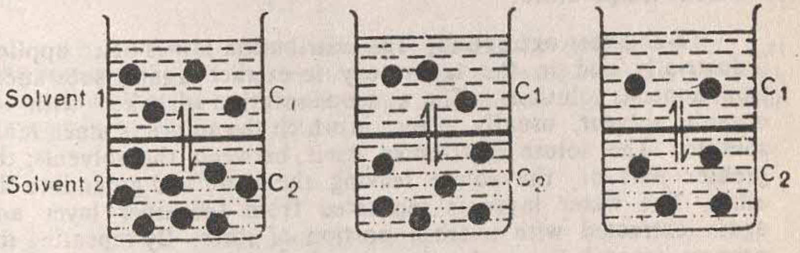
## 12. Distribution Law

Consider a system of two immiscible liquids which are in contact but separated by a phase boundary. When a substance soluble in both liquids is introduced into this system, it distributes itself between the two phases until an equilibrium is established. Experiments show that the distribution of the solute occurs in such a way that its concentration in the two liquids is constant at constant temperature. That is,

$$\frac{\text{Concentration of solute } X \text{ in liquid A, } C_1}{\text{Concentration of solute } X \text{ in liquid B, } C_2} = \text{constant, } K$$

The constant $K$ is called the distribution coefficient or partition coefficient of that system at that temperature. This behaviour is a general one and is known as the *distribution law* or *partition law*. It may be stated as follows :

*A mathematically constant ratio exists between the concentrations of a solute in two immiscible liquids in contact with each other at a constant temperature when equilibrium is established.*



*a* *b* *c*

Fig. 3-32. Diagrammatic illustration of partition law :

(a) $\frac{C_1}{C_2}=\frac{4}{8}=\frac{1}{2}$ (b) $\frac{C_1}{C_2}=\frac{3}{6}=\frac{1}{2}$ (c) $\frac{C_1}{C_2}=\frac{2}{4}=\frac{1}{2}$

*Example.* Iodine is soluble in both water and benzene. If iodine is added to a mixture of water and benzene and the mixture is shaken until equilibrium is attained, the concentration of iodine in benzene layer is always found to be about 400 times as great as that in the water layer at room temperature.

It is important to realize that the partition law refers to the ratio of the *concentrations* of the solute in each phase and not to the ratio of the amounts; the ratio of the amounts of solute will vary with the relative volumes of the two liquids.

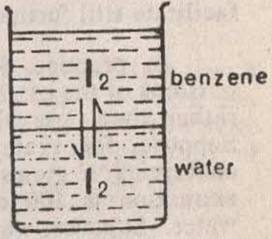


Fig. 3-33. Distribution of iodine in benzene and water.

The distribution law only holds true when the following conditions obtain :

1. The solute is in the same molecular condition in both solvents, *i.e.*, it does not dissociate or associate in either solvent.

2. No chemical combination occurs between the solute and either solvent.

3. The quantity of solute added is not so great that its solubility in either solvent is exceeded.

4. The temperature and pressure remain constant throughout.

5. Equilibrium is reached before the concentrations are compared.

**12-1. Distribution law and Henry's law.** Distribution law is of very wide application and holds for the distribution of a dissolved substance between any two phases, *e.g.*, gas—liquid, liquid—liquid, and liquid—solid. Henry's law for the influence of pressure on the solubility of a gas is really a special case of distribution law involving the distribution of a gaseous solute between free space and the liquid solvent in a constant ratio at constant temperature.

**12-2. Ether extraction.** The distribution law is often applied industrially and in the laboratory to extract organic substances from aqueous solutions. The aqueous solution is shaken with an organic solvent, usually ether, in which the solute is much more soluble. The solute distributes itself between the solvents; the greater part of the solute leaving the water and going into the ether. The water layer is separated from the ether layer and again extracted with a fresh portion of ether. By repeating the process several times the concentration of the dissolved solute in the water solution can be reduced to a negligibly small value. Thus, aniline is usually recovered from a mixture with water by using ether, and penicillin is extracted from a dilute aqueous solution with chloroform. Since, the solubility of organic compounds is lower in aqueous solutions of electrolytes than in pure water, a suitable salt is often added to the water layer to facilitate still further the extraction process.

In practice, it is more efficient to use a number of small portions of the extracting solvent in turn and separating each time, rather than use the same total volume in a single extraction. Suppose, for example, we have one litre of an aqueous solution containing '*a*' grams of solute X, the volume of ether available for extraction is 100 $cm^3$, and X is 20 times as soluble in ether as in water. Suppose, whole of the ether is used in one single extraction where by *w* grams of the solute is extracted and $(a-w)$ grams of the solute remains in aqueous layer.

$$\text{Now, } \frac{\text{Concentration of X in ether}}{\text{Concentration of X in water}}=\frac{20}{1}, \text{ given}$$

Since, concentration is weight per unit volume,

$$\frac{w/100}{(a-w)/1000}=\frac{20}{1}$$

or, $$10w=20a-20w$$

or, $$30w=20a$$

or, $$w=2/3a$$

That is, 66·66 per cent of the solute X is extracted.

Now suppose, the ether is used in two successive volumes of 50 cm$^3$. Let the amonnt of the solute extracted in the first extraction be $w_1$ grams when the amount left in the aqueous layer will be $(a-w_1)$ grams. In this case

$$\frac{w_1/50}{(a-w_1)/1000}=\frac{20}{1}$$

or, $$20w_1=20a-20w_1$$

or, $$40w_1=20a$$

or, $$w_1=\tfrac{1}{2}a \quad ...(i)$$

The amount left in aqueous solution is $(a-\frac{1}{2}a)=0{\cdot}5a$. Let the amount of the solute extracted in the second extraction using 50 cm$^3$ of ether be $w_2$ grams when the amount left in the aqueous layer will be $(0{\cdot}5a-w_2)$ grams. Now,

$$\frac{w_2/50}{(0{\cdot}5a-w_2)/1000}=\frac{20}{1}$$

or, $$20w_2=10a-20w_2$$

or, $$40w_2=10a$$

or, $$w_2=\tfrac{1}{4}a \quad ...(ii)$$

∴ The total amount of solute extracted $=w_1+w_2$

$$=\frac{1}{2}a+\frac{1}{4}a=\frac{3}{4}a$$

that is, 75 per cent of the solute is extracted.

Similarly, it can be shown by means of calculation that if ether is used in four successive instalments of 25 cm$^3$, 80·2 per cent of the solute will be extracted. Using five successive volumes of 20 cm$^3$ of ether will permit the extraction of 83·8 per cent of the solute, and so on.

## 13. Solid-Liquid Systems

The solid-liquid systems are generally studied in vessels open to the atmosphere. So, the pressure variable is fixed at 1 atmosphere, and the degrees of freedom for the systems are reduced by one. As such the phase rule equation for such systems may be modified as

$$F=C-P+1$$

The phase diagrams for such systems are drawn with temperature and composition (usually expressed as weight percentage) as the axes.

**13-1. Lead-silver system.** Silver and lead are completely insoluble in one another in the solid state. In the molten state they mix in all proportions to give homogeneous solutions without forming any compounds. The phases involved in the equilibrium are : (1) solid silver, (2) solid lead, and (3) mutual solution of silver and lead. The gas phase of either metal is ruled out as the boiling points of both metals are very high. Since the composition of the various phases can be represented by two chemical individuals, *viz.*, silver and lead, the silver-lead system is a two component system.

The phase diagram of the silver-lead system is shown in Fig. 3-34. Point A is the freezing point of pure lead (327°C). As increasing quantities of silver are added, the freezing point of lead falls along AE, called the freezing point curve of lead. B is the freezing point of pure silver (961°C). As increasing quantities of lead are added, the freezing point of silver falls along BE, called the freezing point curve of silver.

Along AE solid lead (solid phase) is in equilibrium with the solution (liquid phase) of silver in lead. Similarly, along BE solid silver is in equilibrium with the solution of lead in silver. So, the number of phases along AE and BE each is 2. Applying the modified phase rule

$$
\begin{aligned}
F &= C - P + 1 \\
&= 2 - 2 + 1 \\
&= 1
\end{aligned}
$$

Therefore the system is univariant along AE and BE both. A change in temperature causes a corresponding change in the composition of the liquid mixture (alloy) in equilibrium with the solid

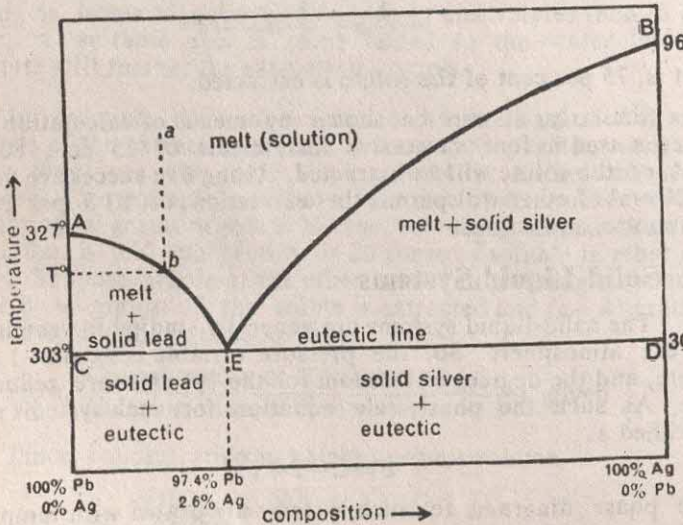


Fig. 3-34. Lead-silver system (not drawn to scale).

metal. Alternatively, a change in the composition of the liquid mixture must be accompanied by a corresponding temperature change. Thus, if either the temperature variable or the composition variable is fixed, the other variable is immediately fixed.

**The eutectic point.** The curves AE and BE meet at the point E. Here, three phases are present in equilibrium, namely, solid lead, solid silver, and the liquid lead-silver alloy. Applying the modified phase rule equation

$$\begin{aligned} F &= C-P+1 \\ &= 2-3+1 \\ &= 0 \end{aligned}$$

Thus, the system at E has no degrees of freedom; it is invariant. This means that these three phases can coexist only at one specific temperature and one definite liquid (alloy) composition. For the lead-silver system, this temperature is 303°C and the composition of alloy is 2·6 per cent of silver and 97·4 per cent of lead. The point E lies at a temperature which is lower than the melting point of either component. It is called the **eutectic point.** *Eutectic point represents the lowest temperature at which a mixture of the two components can exist in the liquid state.* If the liquid mixture is cooled below this temperature, both metals separate simultaneously in the solid state without change of temperature or composition. *A solid solution of two* (or more) *substances having the lowest freezing point of all the possible mixtures of the components is called the eutectic mixture.* The temperature and composition of the alloy corresponding to the eutectic point are called the *eutectic temperature* and the *eutectic composition* respectively.

In the area above the lines AE and BE there exists only one phase, the homogeneous liquid solution of lead and silver. The system is therefore bivariant ($F=C-P+1=2-2+1=2$) and has two degrees of freedom. Therefore, temperature and composition can be varied independently. In order to define any point in this area, therefore, it is necessary to specify the temperature as well as the composition.

When all the homogeneous liquid alloy is changed to a solid mixture of lead and silver at the eutectic point, the temperature begins to fall again. Below the line CED running parallel to the composition axis and passing through the eutectic point, the alloys are completely solid and consist of lead+eutectic or silver +eutectic as shown.

**13·2. Desilverization of lead.** The facts contained in the diagram of the lead-silver system form the basis of the Pattinson's process for the desilverization of lead.

In Fig. 3-34. let *a* represent the molten argentiferous lead containing a very small amount of silver (usually less than 0·1 per cent). On cooling the temperature falls along *ab* and the melt begins to deposit crystals of pure lead at *b* corresponding to the temperature T. At this temperature solid lead and liquid mixture of composition *a* are in equilibrium. On further cooling the system shifts along *b*E, and more lead separates as solid (it is removed from the melt by perforated ladels). Thus the melt becomes progressively poorer in lead and correspondingly richer in sil ver. This continues until the point E is reached. Now the melt has the composition of the eutectic mixture (2·6 per cent of silver) and it all solidifies at the eutectic temperature.* The lead-silver eutectic is subjected to cupellation to remove lead as lead oxide and recover silver.

**13-3. Freezing point curves**. Equilibrium diagrams of the type shown in Fig. 3-34 for the lead-silver system are drawn with the help of a series of freezing point curves of the pure components and their mixtures. To obtain these curves, two pure metals, say A and B, and their mixtures of various compositions are melted by turn and allowed to cool slowly. In each case, temperature is measured at definite time intervals. The observed data are recorded as cooling curves by plotting the time along the abcissa and the temperature along the ordinate axis. The temperature at which the solid begins to separate from each melt is determined by the position of the change in the gradient of each curve. Typical cooling curves are shown in Fig. 3-35.

Curve 1 in Fig. 3-35 is the cooling curve of pure molten metal A. At first the temperature falls uniformly along *ab*. At point *b* the solid phase beings to form, and the curve shows a break. Since solidification is accompanied by the liberation of the latent heat of fusion of the metal, the temperature remains constant until the entire mass of the molten metal has solidified at *c*. The temperature now again decreases uniformly along *cd*. Thus, the portion *ab* represents the cooling of the molten metal A, the horizontal portion *bc* represents the freezing of the melt, and the portion *cd* represents the cooling of the solidified metal. The freezing point of the pure metal is the temperature of the horizontal portion *bc* of the curve. Curve 7, the cooling curve of pure molten metal B, is similar to curve 1.

The addition of pure metal B to the pure metal A in increasing amounts results in a progressive lowering of the freezing point of A as indicated by the points *b*′ in curve 2 and *b*″ in curve 3. As the metal separates, the composition of the alloy remaining in the liquid state changes and its solidification temperature keeps on falling until the crystallization is completed. When the alloy reaches the eutectic composition, the temperature ceases to drop as the eutectic separates at a constant temperature. When the eutectic has completely solidified, the temperature again begins to fall. When molten alloy of eutectic composition (60% A+40% B) is cooled, no solid appears until the eutectic temperature, T. is reached, when the whole mixture freezes sharply depositing both metals simultaneously (curve 4).

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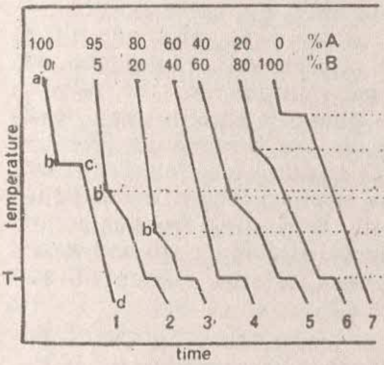
*A mixture richer in silver than the eutectic mixture will deposit pure silver on cooling until the eutectic composition is reached when it will all solidify.

In a similar manner, the addition of increasing amounts of A to the pure metal B causes the freezing point of B to decrease progressively (curves 6 and 5). The cooling curves for all the mixtures of the metals A and B exhibit a common arrest at the eutectic temperature.



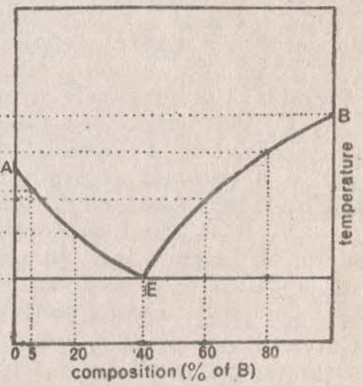


**Fig. 3-35. Cooling curves for pure metals A and B and a series of their alloys; the metals are completely soluble in one another in the liquid state and completely insoluble in one another in the solid state.**

**Fig. 3-36. Equilibrium diagram (temperature-composition diagram) for two metals A and B corresponding to the cooling curves showing in Fig. 3-35.**

Fig. 3-36 shows schematically how an equilibrium diagram of a system of two metals A and B can be constructed from the cooling curves in Fig. 3-35 by plotting the freezing points against composition. The curve AE represents the progressive lowering of the freezing point of pure A by the addition of pure B. The curve BE represents the progressive lowering of the freezing point of pure B by the addition of pure A. The two curves intersect at the point E which represents the composition of the eutectic alloy.

**13-4. Salt-water system.** Many inorganic salts (*e.g.*, sodium chloride, sodium nitrate, potassium iodide, etc.) form eutectic mixtures with water. Since the melting points of salts are much higher than the boiling point of water, it is not possible to represent the melting points of both components.

A typical salt—water equilibrium diagram is shown in Fig. 3-37. A is the freezing point of water — 0°C at 1 atmospheric pressure. On adding salt, the number of components becomes two. Since pressure is constant at the atmospheric value, the vapour pressure of water can be neglected in comparison, and the vapour phase can be ignored. The system, therefore, has two phases : ice and solution of the salt in water (the salt dissolves in the water in contact with ice). Hence, the degrees of freedom

$$F=C-P+1$$
$$=2-2+1=1$$

Thus, for any definite temperature there will be one definite composition of the solution. If the composition of the solution is changed, there will be a corresponding change in temperature. With the progressive addition of the salt, the composition of the solution continually changes and the freezing point of the solution keeps falling along AC. This continues until the concentration of solution reaches a certain definite value at C, when the entire solution freezes into a solid mass. Curve AC, represents the freezing points of progressively stronger solutions of the salt in water. At C, the system has three phases in equilibrium : solid salt, ice, and solution. The point C, therefore, is invariant ($F=2-3+1=0$) at a constant pressure. This is the eutectic point of the system. This is the lowest temperature at which the salt can exist in solution. Or, it is the lowest of all the possible freezing points of solutions of the given salt. In systems involving a salt and water it is often called the *cryohydric point* and the mixture of that particular composition as a *cryohydrate*.*

Curve CB represents the effect of temperature on the 'solid salt—saturated solution' system. It cannot be carried to the 100%

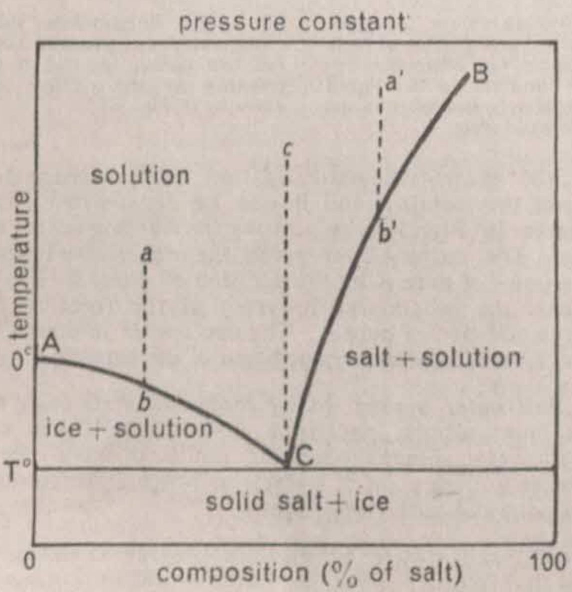


Fig. 3-37. Equilibrium diagram of a salt-water system.

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*The mixture of solid salt, ice, and solution deposited at the eutectic (cryohydric) point was at one time considered to be a definite hydrate of the salt to which the name cryohydrate was given.

salt axis as it comes to an end at the boiling point of the saturated solution.

It may be noted that solutions of salt of varying compositions are in equilibrium with a solid phase along AC and CB both—with ice along AC and with solid salt along CB. Thus, the system is univariant along both the curves. In the area above these curves only the solution phase exists and the system is bivariant.

**Effect of cooling salt solutions**. When a dilute solution of the salt, *i.e.*, less concentrated than eutectic composition, represented by *a* is cooled. the temperature falls along *ab* without any change in composition as the system is bivariant. On reaching *b*, pure ice crystallizes out, and the system becomes univariant Since the concentration of solution increases as the salt crystallizes out, the temperature does not remain constant but keeps falling along *b*C. The crystallization of ice and the lowering of the freezing point continue until the concentration of the solution reaches a certain definite value for each given solute, represented by the eutectic point C. Now, the entire solution freezes into a solid eutectic mixture consisting of thin layers of ice and solute in the solid form. The temperature at this point, T°, is the lowest temperature that can be attained in this system. It is called the *eutectic temperature* of the system.

If a solution of composition *a′*, containing a higher concentration of salt than the eutectic is cooled, the solid salt begins to crystallize at *b′*. As the salt keeps falling out, the concentration of the solution progressively decreases, and the system moves down along BC. At C, the eutectic point, the entire solution freezes to give the eutectic mixture or the cryohydrate.

Thus, all solutions—more dilute or concentrated than eutectic composition—ultimately show on arrest at the eutectic point. In dilute solutions this point is reached with the ice separating out first and in concentrated solutions with the solid salt separating out first. If a solution of the eutectic composition represented by *c* (vertically above the eutectic point C) is cooled, the temperature falls along *c*C without any change in composition. When the eutectic point C is reached, both ice and solid salt separate out simultaneously.

**Freezing mixtures**. When a salt is added to melting ice, some of the salt dissolves in the water. This gives rise to system containing three phases—solid salt, ice, and salt solution. Such a system, however, can exist in stable equilibrium only at the eutectic point which is, in most cases, considerably lower than the normal melting point of ice. So, the ice melts and the salt dissolves in the water produced. Both of these processes absorb heat and continue until the temperature falls (along AC in Fig. 3-37) to the eutectic temperature, or until one of the solids is all used up. The lowest temperature that can be attained in a salt-ice mixture depends upon the eutectic temperature of the system. The same minimum temperature can also be attained by adding ice to a saturated solution of salt, when the temperature well fall along BC in Fig. 3-37.

The eutectic temperatures for a few salt-ice mixtures are :

| | |
|---|---|
| (1) NaCl+ice.........−22°C | (2) $CaCl_2$+ice........−56°C |
| (3) $NH_4Cl$+ice........−16°C | (4) $NaNO_3$+ice......−18°C |
| (5) $NH_4NO_3$+ice......−18°C | (6) KI+ice..........−23°C |

## 14. Chromatography

Chromatography is a general term for any technique of separating compounds based on the differences in their distribution between two immiscible phases, one of which is the *stationary phase* with a well developed surface area, and the other is the *mobile phase*, *e.g.*, a liquid stream flowing through the stationary phase. A chromatographic method is called *adsorption chromatography* if the stationary phase is a soild and *partition chromatography* if the stationary phase is a liquid.

Common chromatographic methods include column chromatography, thin layer chromatography, paper chromatography, and gas chromatography.

**14-1. Column chromatography.** This technique is based on the difference in adsorption of various components on a solid. It consists in allowing a solution of a mixture in a suitable solvent to flow down a column packed with a highly adsorbing material, *e.g.*, alumina and passing pure solvent through the column after the solution has been charged. The more strongly adsorbed components of the mixture tend to be retained near the top of the column while others move down to various distances, depending on the extent to which they are absorbed and how much pure solvent is run afterwards. If the mixture consists of coloured substances, the packing of the column is separated into as many coloured zones (after complete separation) as the number of components.

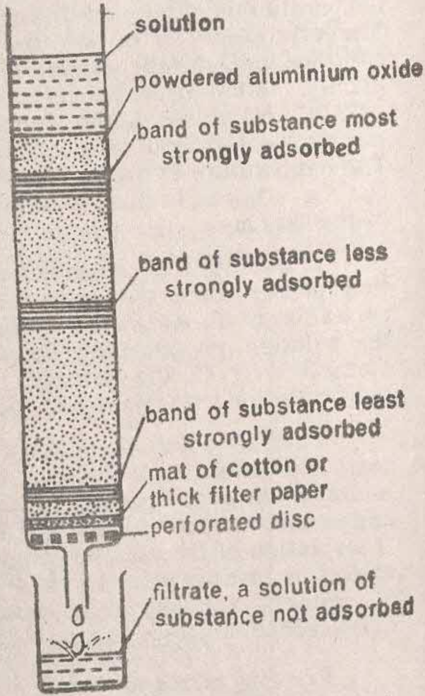
solution
powdered aluminium oxide
band of substance most strongly adsorbed
band of substance less strongly adsorbed
band of substance least strongly adsorbed
mat of cotton or thick filter paper
perforated disc
filtrate, a solution of substance not adsorbed

Fig. 3-38. Column chromatography.

**14-2. Thin layer chromatography**. This technique differs from column chromatography in that the long vertical column of adsorbent material is replaced by a flat glass plate coated with a thin layer of the adsorbent. The solvent (mobile phase) moves up the adsorbent layer by capillary action whereby the components of the mixture are separated.

**14-3. Paper chromatography**. In paper chromatography strips of special filter paper with a high moisture content are used in place of a column. A spot of test solution is applied near one end of the paper strip and allowed to dry up. The strip is then suspended vertically in a tightly closed container with the spotted end immersed just up to the spot in a shallow layer of mixed water and organic solvents. The solvent from the shallow layer rises through the paper by capillary action carrying along the various component of the sample. Different components are distributed to differing extents between the stationary paper-bound water and mobile organic phases, and soon located at different positions along the paper. These are detected as coloured spots by spraying the paper strip with reagents which produce colour reactions with them. These reagents are called 'visualizing reagents'. For example, the visualizing reagent in the paper chromatographic separation of As (III) and Sb (III) ions is ammonium sulphide, $(NH_4)_2S$, solution. This reagent detects arsenic as a yellow spot and antimony as an orange spot (by the formation of the corresponding sulphides).

**14-4 Gas chromatography**. The apparatus used in gas chromatography consists of a long narrow tube packed with an inert support material of uniform particle size, *e.g.*, diatomaceous earth.* The support material is coated with a thin film of a non-volatile liquid which constitutes the stationary phase. The whole tube and its contents are maintained at a constant temperature in a thermostatically controlled oven. The sample to be analyzed is carried through the tube by an inert gas (mobile phase) such as argon. The progress of various components of the mixture through the tube is selectively affected by the stationary phase. As a result, some components pass through the tube more rapidly than others.

**14-5. Usefulness of chromatography**. Various chromatographic techniques have proved to be highly successful in separating mixtures of related chemical compounds into their components without drastic chemical or physical treatment. Chromatographic techniques are used to separate ionic and molecular species, polar and non-polar molecules, and geometrical and optical isomers. Gas chromatography provides a very sensitive method of analysing the components of a complex mixture of volatile compounds. In chemical industry, chromatographic techniques are employed to make purest preparations of various vitamins, hormones, penicillin and other antibiotics, etc.

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*Diatomaceous earth, also called kieselguhr, is a mass of hydrated silica ($SiO_2$) formed from skeletons of minute unicellular plants called diatoms. It is a very porous and adsorbent material.

## Questions

1. Define the terms : system, phase, component, and degree of freedom pertaining to phase equilibria.

2. Give the number of phases and components in the following systems, giving reasons for the number of components :

(*i*) Ice—water—steam.

(*ii*) Rhombic sulphur—monoclinic sulphur—liquid, sulphur—sulphur vapour.

(*iii*) Ammonium chloride—ammonia—hydrogen chloride.

(*iv*) Calcium carbonate—calcium oxide—calcium oxide.

3. (*a*) Explain with a suitable example the meaning of the term 'degree of freedom'.

(*b*) State phase rule.

(*c*) With the help of phase rule calculate the number of degrees of freedom of systems in question 2.

4. (*a*) What is evaporation ? Explain the fact that the vapour and the liquid from which the vapour is formed are both at the same temperature although the molecules escaping as vapour possessed higher kinetic energies.

(*b*) What is meant by the term 'vapour pressure of a liquid' ? Show by means of suitable curves the variation of vapour pressure with temperature for two liquids. Apply phase rule to show that a liquid-vapour system in equilibrium is univariant.

5. Define the term 'boiling point'. How is it related to the external pressure against the liquid ? What are the main factors on which the boiling point of a liquid depends ?

6. Explain the reason :

(1) The vapour pressure of a liquid increases as the temperature increases.

(2) At any temperature, the vapour pressure of water is lower than that of ethyl alcohol and of ethyl alcohol lower than that of diethyl ether.

7. Discuss the application of phase rule to the equilibrium between the different phases of water.

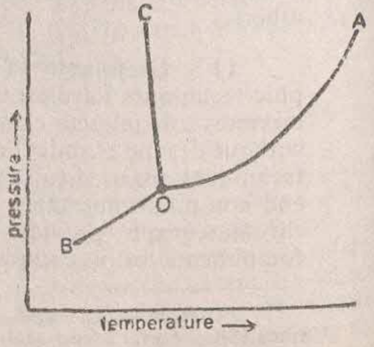
8. The figure in the margin shows the phase diagram of water.

(*i*) What processes are represented by the curves OA, OB, and OC ?

(*ii*) What will happen if the temerature is maintained at a constant value above the triple point and the pressure is progressively reduced ?

(*iii*) What is the temperature corresponding to the point C ?

(*iv*) What is indicated by the incline of the line OC to the left ? Is it so in the phase diagrams of all substances ?



(v) Is it possible to extend the curve OA beyond A? Give reason for your answer.

9. Draw a phase diagram of water. Locate the various equilibria on the diagram and calculate the degree of freedom for each equilibrium.

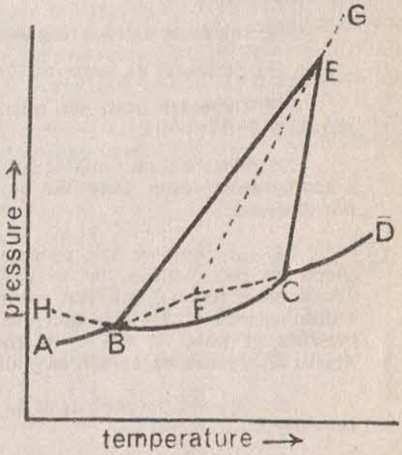
10. What is meant by (*a*) monotropy, (*b*) enantiotropy? Explain the characteristic features of each by reference to the allotropy of sulphur and phosphorus.

11. State phase rule. Draw and discuss the phase diagram of either the sulphur system or the phosphorus system.

12. (*i*) Name the various phases in the sulphur system.

(*ii*) In the phase diagram of sulphur given in the margin, name the various triple points and the phase equlibrium obtaining at each one.

(*iii*) How do you know from the phase diagram of sulphur that all the four phases of sulphur cannot be in equilibrium with each other simultaneously?



13. What variables must be fixed for completely defining the system resulting from physical dispersion of gases in liquids?

14. State Henry's Law. Would this law hold closely for the solubility of the very soluble hydrogen chloride in water? Of the slightly soluble nitrogen in water?

15. How could you increase the solubility of carbon dioxide in water? How decrease it? What causes aerated drinks to effervesce when the cap is removed? Why should the effervescence be less when the aerated drink is cold?

16. How may gases be expelled from their liquid solvents?

17. Explain the Henry's Law in terms of Le Chatelier's principle.

18. (*a*) What is the energy change when a gas dissolves in a liquid?

(*b*) When a glass of cold water is left to stand in a warm room, gas bubbles are observed to form. Explain.

(*c*) When a solution of ammonia in water is boiled for some time in air, the dissolved gas is completely expelled and pure water is left behind. Does this mean that the solubility of ammonia in water at the boiling point of water is nil? Give reasons for your answer.

19. What is meant by 'miscible liquids' and 'immiscible liquids'? Give examples.

20. What are 'ideal solutious' and 'non-ideal solutions' with reference to solutions of liquids in liquids?

21. What is meant by fractional distillation? What condition must obtain to make fractional distillation possible?

22. In which type of liquid-liquid solutions can the components be completely separated by fractional distillation ? Give one example of such a solution.

23. Why is it not possible to obtain 100 per cent sulphuric acid by the fractional distillation of dilute sulphuric acid ?

24. Why is it not possible to obtain 100 per cent ethyl alcohol by the fractional distillation of aqueous ethyl alcohol ?

25. Give four examples of partially miscible liquid pairs. What is meant by the 'critical solution temperature' ?

26. Give one example each of pairs of partially miscible liquids in which the mutual solubility—

(*a*) increases on lowering the temperature,

(*b*) decreases on lowering the temperature,

(*c*) increases both on raising and lowering the temperature beyond certain definite points.

27. When a liquid mixture of two immiscible liquids is heated, it boils at a temperature lower than the boiling point of either pure liquid. Explain the phenomenon.

28. (*a*) Describe the process of steam distillation. (*b*) Which factors affect the compostiion, by weight, of the distillate ? (*c*) For what kinds of substances is steam distillation specially valuable ? (*d*) A mixture of water and bromobenzene ($C_6H_5$ Br) boils at 95.3°C. At this temperature, the vapour pressure of water is 641°C. If the weight of water distilled over be 25 g, what weight of bromobenzene will have distilled ? [Ans. 40.5 g.]

29. Explain the process of an ionic solid, *e.g.*, sodium chloride, dissolving in water.

30. Define the terms : saturated solution, unsaturated solution, supersaturated solution.

31. If a clear solution of sodium thiosulphate ($Na_2S_2O_3$) were given you to test, how could you find whether it was unsaturated, saturated, or supersaturated ?

32. How can you show that the opposite processes of dissolution and crystallization occur side by side in a saturated solutiod in contact with the solid solute ?

33. Define *solubility*. What is the usual effect of temperature changes on the solubility of solids in liquids ?

34. A solution of potassium nitrate is saturated at 65°C. What would you observe and what is the explanation in each of the following cases ? (*a*) A crystal of potassium nitrate is dropped into the solution at 65°C. (*b*) The solution is heated to 75°C, and a crystal of potassium nitrate is added. (*c*) The solution is cooled to 50°C.

35. Heat is observed when a certain solid is dissolved in water. How will an increase in temperature affect the solubility of the solid ?

36. What are the factors which affect the rate of solution of a solid in a liquid ?

37. (*a*) If you were in a hurry to dissolve some sodium chloride, would you use cold water or hot ? Use the salt in a lump or as a powder ?

(*b*) Salt solutions are heavier than water. To dissolve commercial quantity of a salt without the expense of heating or stirring, would it be better to place the solid on a perforated shelf near the top or at the bottom of the vat ?

39. What are solubility curves ? What is indicated by a sharp break in a solubility curve ?

40 In the following statements, correct those which are wrong :

(*a*) "A saturated solution is one in which no more solute can dissolve".

(*b*) "The volume of a gas which dissolves in a given volume of liquid at constant temperature is directly proportional to the pressure of the gas."

41. Explain the process of fractional crystallization.

41. Draw a fully labelled diagram for the lead-silver system. What is meant by the *eutectic point* ? With the help of the equilibrium diagram of the lead-silver system explain the process for the desilverization of lead.

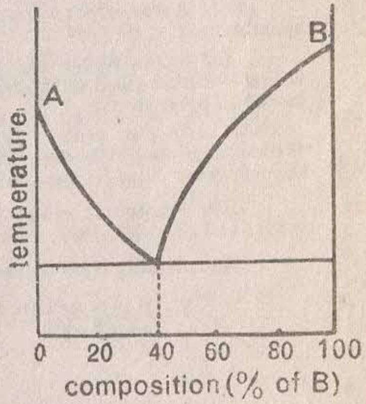
42. Draw the cooling curves you would get on cooling to solidification completely liquid systems of composition (1) one pure compond, A (2) the eutectic composition of A and B, and (3) a composition between (1) and (2). Explain each curve. Draw an equilibrium diagram for the system A—B corresponding to these cooling curves.

43. Study the equilibrium diagram of the system A-B given in the margin.

(*a*) Which metal will first separate on cooling a molten alloy containing 50 per cent A and 50 per cent B ?

(*b*) How many grams of this metal will separate out of 100 g of the alloy before the eutectic is reached ?

[Ans. (*a*) B, (*b*) 16.67 g]



44. (*a*) Draw a phase diagram for the water-salt system. Label it fully to bring out the main points of information about the various equlibria.

(*b*) What will be the effect of cooling a salt solution which is (1) less concentrated, (2) more concentrated than the eutectic composition ?

(*c*) Explain briefly the theory of freezing mixtures.

45. (*a*) State the *distribution law*. Under what conditions does this law hold good ?

(*b*) Explain why in the process of extraction, the extracting solvent should be used in small lots rather than using the whole liquid in one lot.

46. (*a*) What is chromatography ?

(*b*) What is the main difference between adsorption chromatography and partition chromatography ?

47. (*a*) Name the common methods of chromatography.

(*b*) Describe column chromatograhpy with the help of a suitable diagram.

(*c*) Describe the usefulness of chromatographic methods.

## Key

2. (*i*) 3 phases, 1 component (*ii*) 4 phases, 1 component (*iii*) 2 phases, 1 component (*iv*) 2 phases, 2 components

6. (2) This is because the intermolecular attractive forces are smallest for ether and greatest for water.

8. (*iv*) The slight incline of the line OC to the left shows that the melting point of water is lowered by raising the pressure. This is not so in the phase diagrams of most substances since, usually, the melting point increases as the pressure is increased.

(*v*) NO, the curve OA cannot be extended beyond A because at higher temperatures the liquid and vapour are indistinguishable.

9. See Table 3-1, page 71.

11. (*iii*) Because there is no point where any four curves meet together.

13. Two variables : temperature and pressure.

15. The solubility of carbon dioxide in water can be increased by (*i*) increasing the pressure, and (*ii*) lowering the temperature. The solubility can be decreased by (*i*) decreasing the pressure, and (*ii*) increasing the temperature. The effervescence in aerated drinks upon uncapping the bottle results from a decrease in pressure to 1 atm. The effervescence is less when the aerated drink is cold as the solubility of the dissolved carbon dioxide is more at lower temperature.

18. (*a*) Heat is evolved.

(*b*) As the water warms to room temperature, the dissolved air escapes as bubbles.

(*c*) The inference that the solubility of ammonia in water at 100° is nil is wrong since the gas is not in equilibrium with the solution when the solution is boiled in open air.

28. (*d*) *The vapour pressure of [bromobenzene at 95·3°C = 760 mm— 641 mm = 119 mm. (because, the sum of the vapour pressures of water and bromobenzene must be equal to the atmospheric pressure, 760 mm).*

The molecular weight of bromobenzeue, $C_6H_5Br$, is $6\times12+5\times1+80=157$, and of water, $H_2O$, $=18$.

Substituting these values in the relation

$$\frac{\text{wt. of bromobenzene}}{\text{wt. of water}}=\frac{\text{vap. pressure of bromobenzene}}{\text{vap. pressure of water}}\times\frac{\text{mol. wt. of bromobenzene}}{\text{mol. wt. of water}}$$

$$\frac{\text{wt. of bromobenzene}}{25g}=\frac{119\ mm}{641\ mm}\times\frac{157}{18}$$

$$\therefore\ \text{weight of bromobenzene}=25\ g\times\frac{119\ mm}{641\ mm}\times\frac{157}{18}=40{\cdot}5\ g.$$

31. By placing a small crystal of sodium thiosulphate in the solution. If it dissolves, the solution is unsaturated; if it does not dissolve, the solution is saturated; if the crystallization sets in instantaneously, the solution is supersaturated.

32. (*a*) The crystal will remain undissolved.

(*b*) The crystal will dissolve.

(*c*) Some potassium nitrate will separate from the solution as crystals.

35. The solubility of the solid will descrease on increasing the temperature.

37. (*a*) Hot water; as a powder.

(*b*) It will be better to place the solid on a perforated shelf near the top. The salt from the immersed surface will dissolve in the surrounding water and the denser solution thus formed will sink to the bottom allowing fresh water to dissolve out more of the salt. If the solid is placed at the bottom of the vat, it will soon be surrounded by its saturated solution in water, and no further dissolution of the solid will occur.

38. A solubility curve is a graphical representation of the relationship of solubility and temperature for a given solid. A sharp break in the solubility curve indicates the formation of a hydrate of the solute of a different composition.

39. Both statements are wrong. The corrected statements are :

(*a*) A saturated solution is one in which no more solute can disslove at a specified temperature.

(*b*) The volume of a gas which dissloves in a volume of liquid at constant temperature is independent of pressure.

Or,

The weight of a gas which dissolves in a given volume of liquid at constant temperature is directly proportional to the pressure of the gas.

43. (*a*) The temperature at which the alloy begins to solidify lies on the cooling curve of B corresponding to 50% B. Therefore, on cooling the molten alloy B will first crystallize out and will continue to separate until eutectic composition is reached.

(*b*) 100g of the alloy contains 50g of A and 50g of B. The eutectic A-B contains 60 per cent B. Therefore all of B, *i.e.*, 50g of B, must remain in the eutectic. Since the eutectic contains 60 parts of B for 40 parts of A, the amount of A corresponding to 50g of B in the eutcetic is $\frac{40}{60} \times 50\text{g} = 33{\cdot}33\text{g}$.

Therefore, the amount of B that will separate out before the eutectic forms is $50\text{g} - 33{\cdot}33\text{g} = 16{\cdot}67\text{g}$.

□

## 4

# Colloidal Solutions

Graham (1861) classified substances as *crystalloids* and *colloids* depending on whether their particles in solution could diffuse through vegetable or animal membranes. The former group included crystalline solids such as common salt, sugar, and urea; the latter group included substances which usually exist in amorphous or gelatinous condition, such as starch, gelatine, and glue. The word 'colloid' is derived from two Greek words *Kolla* (glue) and *eidos* (like), and suggests 'like glue'. It is now known, however, that a colloid is not a particular class of substances but a substance in a certain state of sub-division. Any substance may be obtained in a colloidal condition if suitable means are employed, although some substances assume it more readily than others. Hence, it is more precise to use the term 'colloid' in reference to a state of matter rather than a kind of matter. In fact, the same substance can behave like a colloid in some solvents and like a crystalloid in others. For example, ordinary soap dissolved in water does not penetrate a membrane, showing it to be a colloid; the same soap in alcohol solution possesses the properties of a crystalloid.

Many naturally occurring substances such as milk, blood, rubber, clouds, fogs, mist, coloured gems, etc., are colloidal in nature. This is what makes the study of colloidal state a branch of Chemistry of much practical significance.

## 1. True Solutions, Colloidal Solutions, and Suspensions

Any system made up of a substance distributed or scattered as minute particles* through another substance is called a *dispersion system*; the distributed substance is known as the *dispersed phase* (or, the *internal phase*) and the continuous medium around it as the *despersion medium* (or, the *external phase*). Depending on the degree of dispersion, the dispersion systems are classed as true solutions, colloidal solutions, and suspensions. In most common systems, the dispersed phase is a solid and the dispersion medium a liquid.

A *true solution* is a system with a very high degree of dispersion in which the distributed substance exists as molecules or ions. As such there is no dispersed phase in a true solution, and the entire system is one single phase.

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*The particles of the dispersed substance may be very fine particles of a solid, minute droplets of a liquid, or extremely tiny bubbles of a gas.

A *colloidal solution* is a system in which the size of the dispersed particles is much larger than in true solutions but still too small to be observed by means of an ordinary microscope or detained by an ordinary filter paper A colloidal solution, therefore, appears homogeneous and usually as clear as a true solution and, like it, filters unchanged through a filter paper. However, unlike a true solution, colloidal solution is characterized by the presence of two distinct phases.

A *suspension* consists of particles of a solid, large enough to be visible under a microscope or even to the naked eye, suspended in a liquid medium. Like a colloidal solution, a suspension, too, has two distinct phases but, unlike it, it is not a stable system and can exist for a limited time only, until the suspended particles settle out. The particles of the dispersed phase in a colloidal solution do not tend to settle out and can remain indefinitely suspended in the dispersion medium. A colloidal solution of gold prepared by Faraday over a century ago continues to be in excellent condition even today.

**1-1. The range of colloidal size.** The particles of a colloid are midway in size between the solute particles of molecular or ionic dimensions in true solutions and the particles in suspensions even the smallest of which are visible under microscope. In most ordinary solutions the particles of solute are less than $10^{-7}$cm in diameter, but in a colloidal solution, the particles range from about $10^{-7}$ cm to about $2 \times 10^{-5}$ cm across. They are too small, therefore, to be, seen under an ordinary microscope or to be separated by filtration. Colloidal particles are usually aggregates of hundreds or even thosuands of molecules. However, some colloids, *e.g.*, proteins and viruses* consists of single well defined molecules. When the particle size is more than $2 \times 10^{-5}$ cm the resulting system is a suspension.

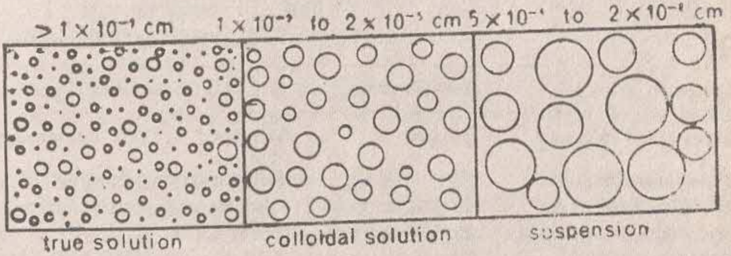

Fig. 4-1. Particle size ranges in true solutions, colloidal solutions, and suspensions.

**1-2 Comparison of the characteristic properties of true solutions, colloidal solutions, and suspensions.** It must be appreciated that no sharp boundary can be drawn between colloidal solutions and true solutions on one hand, and the colloidal solutions and suspensions on the other. A comparison of the characteristic properties of these three classes of dispersion systems is made in Table 4-1.

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*Viruses, known to be large protein molecules, may have giant molecules with molecular weights ranging from several hundred thousand up to millions.

**Table 4-1** *Characteristic properties of true solutions, colloidal solutions, and suspensions*

| *Property* | *True solution* | *Colloidal solution* | *Suspension* |
|---|---|---|---|
| 1. Particle size (diameter) | Less than $10^{-7}$ cm | $10^{-7}$ cm to $2 \times 10^{-5}$ cm | More than $2 \times 10^{-5}$ cm |
| 2. Appearance | Clear and homogeneous | Generally clear and homogeneous | Opaque and heterogeneous |
| 3. Nature | Homogeneous, stable, one phase system | Heterogeneous, stable, two-phase system | Heterogeneous, metastable, two-phase system |
| 4. Separation by filtration | Not possible | Not possible | Possible |
| 5. Visibility of particles | Not visible even under ultramicroscope | Visible under ultramicroscope | Visible to naked eye or under microscope |
| 6. Tendency of particles to settle out | Totally absent | Insignificant | Strong; varies with actual size of particles |
| 7. Brownian movement | Not observable | Occurs | May occur |

**1-3. Types of colloidal systems.** A colloidal system is a two-phase system, and each one of the two phases can be in any one of the three physical states of matter —gas, liquid, and solid. Thus, in all there could be nine possible types of dispersions. However, a colloidal system of *gas-in-gas* cannot form since all gases consist of molecules and molecules of one gas mix in all proportions with molecules, of another gas producing a single phase. The eight possible types of colloidal systems are listed in Table 4-2.

**Table 4-2** *Types of colloidal systems*

| *Type* | *Common name* | *Examples* |
|---|---|---|
| 1. Gas dispersed in liquid | Foam | Whipped cream, beaten egg white |
| 2. Gas dispersed in solid | | Pumice stone, floating soaps |
| 3. Liquid dispersed in gas | Liquid aerosol | Clouds, fogs, mists, sprays |
| 4. Liquid dispersed in liquid | Emulsion | Milk, butter |
| 5. Liquid dispersed in solid | Gel | Jellies, pearl ($H_2O$ in $CaCO_3$) |
| 6. Solid dispersed in gas | Solid aerosol | Smoke, dust |
| 7. Solid dispersed in liquid | SOL | Starch suspension, inks, paints |
| 8. Solid dispersed in solid | Solid sol | Coloured gems, some alloys |

The most important colloidal systems are those in which a solid is dispersed in a liquid. Such systems are called colloidal solutions or **sols**. Colloidal solutions in water are known as *hydrosols* and those in alcohol as *alcosols.*

## 2. Lyophilic and Lyophobic Colloids

Colloids are classified as *lyophilic* ("liquid-loving") and *lyophobic* ("liquid-hating") according as their relative attraction for the dispersion medium is strong or weak. In particular, when the dispersion medium is water, the colloids may be *hydrophilic* ("water-loving") or *hydrophobic* ("water-hating"). Hydrophilic colloids include starch, glue, gums, proteins, and generally high-molecular weight compounds; hydrophobic colloids are, for the most part, elements or compounds of an inorganic character, *e.g.*, metals, metal sulphides, sulphur, etc.

On evaporation hydrophilic sols form jelly-like solids which again disperse to form the sol upon addition of water. Hence, hydrophilic sols are often termed '*reversible sols*'. The reason of this behaviour is that the hydrophilic colloids have a strong attraction for water and tend to become extensively hydrated. In this process water gets trapped in such a way that the viscosity of the system increases. That is, the sols of lyophilic colloids are much more viscous than the pure solvent.

When water is removed from a hydrophobic sol, the solid material left behind is not reconverted into the sol by the simple addition of water. The hydrophobic sols are, therefore, often termed '*irreversible sols*'. The viscosity of the sols of hydrophobic colloids is the same as that of water for two obvious reasons. First, water can disperse only a small amount of a hydrophobic colloid and, hence, its concentration in the sol is low. Secondly, the hydrophobic colloids have negligible attraction for water.

Hydrophilic and hydrophobic colloids differ in several other respects. A comparison of their properties will be made later in Section 6.

## 3. Preparation of Colloidal Solutions

**3-1. Preparation of hydrophilic sols.** Some substances, such as starch, gelatine, gums, proteins, etc., form colloidal solutions when warmed with or left in contact with water for a sufficient length of time The particles are already of colloidal size and they spontaneously disperse in the water forming colloidal solutions.

**3-2. Preparation of hydrophobic sols** The preparation of hydrophobic sols consists of bringing the solid to be dispersed in water in the form of particles of colloidal size. The methods available are of two main types : (*a*) condensation, and (*b*) disintegration or dispersion.

A. **Condensation methods**. In condensation methods particles of colloidal size are produced by growth from smaller units, such as molecules or ions. These methods usually employ chemical reactions such as decomposition, oxidation, reduction, double decomposition, and hydrolysis taking place in aqueous solutions, and in some cases, exchange of solvent.

1. *Decomposition.* This method is exemplified by the formation of sulphur sols when a few drops of an acid are added to a dilute solution of sodium thiosulphate. The insoluble free sulphur produced by the decomposition of sodium thiosulphate accumulates into small clusters. These small clusters of sulphur impart various colours— blue, yellow and even red to the system, depending on their growth within the colloidal size range.

$$\underset{\text{thiosulphate}}{S_2O_3^{2}} + \underset{\text{acid}}{2H^+} \longrightarrow \underset{\text{sulphur}}{S\downarrow} + H_2O + SO_2\uparrow$$

2. *Oxidation.* Sulphur sols are also made by the oxidation of hydrogen sulphide in aqueous solutions by means of hydrogen peroxide, sulphur dioxide, nitric acid, etc.

$$H_2S+H_2O_2 \rightarrow 2H_2O+S\downarrow$$
$$2H_2S+SO_2 \rightarrow 2H_2O+3S\downarrow$$
$$H_2S+[O] \rightarrow H_2O+S\downarrow$$

3. *Reduction.* Metal sols are best made by reducing solutions of their salts by suitable reducing agents. For example, a gold sol is easily produced by reducing the gold (III) ion (in chlorauric acid, $HAuCl_4$) by such reducing agents as formaldehyde, iron (II) sulphate, or tin (II) chloride [$Au^{3+}+3e^- \rightarrow Au^\circ\downarrow$].

$$\underset{\text{gold (III) ion}}{2Au^{3+}} + \underset{\text{tin (II) ion}}{3Sn^{2+}} \longrightarrow \underset{\text{free gold}}{2Au^\circ\downarrow} + \underset{\text{tin (IV) ion}}{3Sn^{4+}}$$

In such reactions gold is set free first in the form of individual atoms which combine into larger aggregates immediately afterwards.

4. *Double decomposition.* Sols of metal sulphides and other insoluble salts (*e.g.*, AgBr) are usually prepared by double decomposition. Thus, a colloidal solution of arsenious sulphide is produced by passing hydrogen sulphide through a cold saturated solution of arsenic (III) oxide in water.

$$As_2O_3 + 3H_2S \rightarrow As_2S_3\downarrow + 3H_2O$$

The resulting arsenious sulphide sol is bright golden yellow.

5. *Hydrolysis.* The preparation of iron (III) hydroxide sol provides an example of this method. When a concentrated solution of iron (III) chloride is added to boiling water, iron (III) hydroxide is produced by hydrolysis.

$$Fe^{3+} + (3Cl^-) + 3H_2O \rightarrow Fe(OH)_3\downarrow + 3H^+ + (3Cl^-)$$

Though iron (III) hydroxide is insoluble in water, it does not form a precipitate under these conditions, but remains suspended in water as colloidal particles. The result is a transparent $Fe(OH)_3$ sol of the colour of strong tea.

6. *Change of solvent.* A substance is often thrown out of solution in particles of colloidal size by suddenly changing the solvent. For example, when alcoholic solutions of sulphur or phosphorus are poured into a large excess of water, in which these substances are only very slightly soluble, they form their respective hydrosols.

**B. Disintegration or dispersion methods**. In the disitegration methods, as the name suggests, particles of colloidal size are produced by the disintegration of a bulk quantity of material. These methods may involve the use of such mechanical methods as grinding or shaking, an electric arc, or the addition of a third substance.

*1. Mechanical grinding*. Coarse particles may be reduced to colloidal size by grinding them with a mortar and pestle. In large scale preparations, large grinding and shearing machines, called *colloid mills*, are used to break down coarse particles to the desired colloidal size. In the colloidal mill (Fig. 4-2), two or more circular discs, nearly touching each other, rotate at high speed, each in the opposite direction to its neighbour. A suspension of the solid in the dispersion medium is slowly fed into the space between the discs. The suspended particles are subjected to a powerful shearing force and are disintegrated to yield particles of colloidal size. Colloid mills are widely used in the industrial preparation of paints, pharmaceutical products, and food products, and for grinding cement *clinker* to produce cement.*

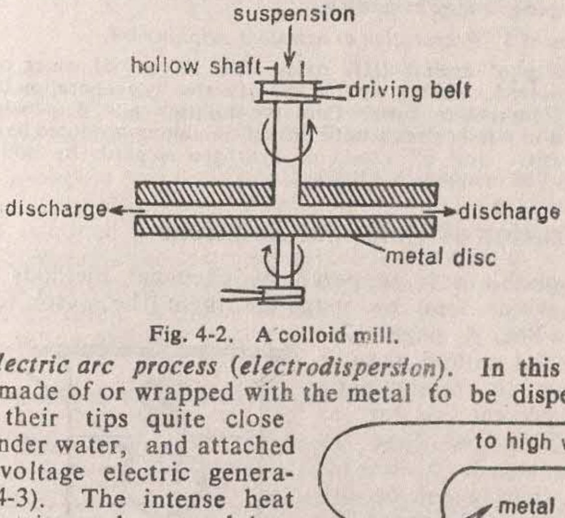

Fig. 4-2. A colloid mill.

2 *Electric arc process (electrodispersion)*. In this process, two wires made of or wrapped with the metal to be dispersed are set with their tips quite close together under water, and attached to a high-voltage electric generator (Fig. 4-3). The intense heat of the electric arc thus struck between the wires causes the metal to vaporize. The vapour immediately condenses to particles of colloidal size producing the metal sol. This method is widely used for the preparation of sols of gold, platinum, silver, copper, and many other metals. It is often referred to as *Bredig's arc method*.

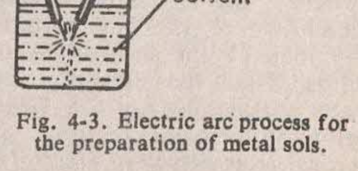

Fig. 4-3. Electric arc process for the preparation of metal sols.

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*The final hardness of concrete depends largely on the fineness of the cement particles.

3. *Peptization*. Freshly precipitated substance may often be reconverted into the colloidal particles which coagulated to form the precipitate, by the addition of a suitable reagent. The process is known as peptization and the reagent added is called the *peptizing agent or dispersing agent*. The peptizing agent is usually an electrolyte having one ion common with the precipitate to be dispersed. For example, freshly precipitated iron (III) hydroxide, obtained by the interaction of iron (III) chloride and ammonium hydroxide, is peptized upon addition of iron (III) chloride solution to form a dark reddish-brown sol.

**Experiment 1.** *Preparation of starch sol.*

Grind about 1g of a *soluble* starch into a thin paste with cold water. Pour the paste drop by drop into about 100 cm$^3$ of water boiling in a beaker. Continue to boil for two minutes after the entire paste has been added. Allov to stand until cold, and then decant off the clear liquid. This is starch sol.

**Experiment 2.** *Preparation of sulphur sol.*

Bubble hydrogen sulphide through distilled water until saturated solution is obtained. Add a few drops of hydrogen peroxide to the solution; it will turn pale-white owing to the formation of colloidal sulphur. Remove the excess of hydrogen sulphide by boiling.

**Experiment 3.** *Preparation of arsenious sulphide sol.*

Boil 0·2 g of arsenic (III) oxide with 100 cm$^3$ of water until it is completely dissolved, making up the loss of water by evaporation by adding distilled water from time to time. Cool the solution and pass hydrogen sulphide through it in a slow stream until the yellow colour produced has acquired maximum intensity. Boil off excess of hydrogen sulphide by boiling. The resulting bright yellow liquid is $As_2S_3$ sol.

## 3. Stabilization of Colloidal Solutions

Hydrophobic sols prepared by chemical methods contain electrolytes which tend to coagulate them (the reason for this is discussed in Sec. 4, page. 123 To stabilize the colloid, then, it is necessary to remove any electrolyte present so far as possible. This is done by placing the sol in a bag of cellophane, parchment, or animal membrane, and suspending the bag in a vessel in which water is being continually renewed. The semipermeable membrane of the bag permits the ions of the electrolyte to diffuse from the sol into the water outside, but not the larger colloidal particles which remain behind in the bag (Fig. 4-4). *The process of separation of colloids in a sol from dissolved electrolytes by selective diffusion through a semi-permeable membrane is called dialysis.* By allowing this process, which is slow, to continue for a time, most of the ions can be eventually removed, and the colloidal sol is thus stabilized.

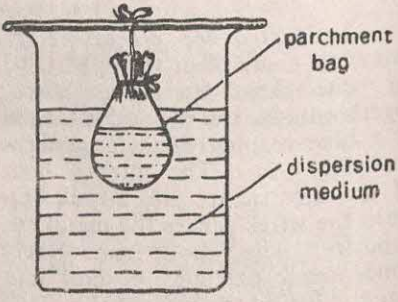

Fig. 4-4. Dialysis.

The process of *ultrafiltration* is also employed for freeing a sol from dissolved electrolytes. This process makes use of *ultrafilters* which are made by impregnating filter paper with collodion solution of a suitable concentration. The ultrafilter of suitable pore size is fitted to a support in such a manner that the sol to be filtered may be subjected to high pressures. Ultrafiltration is more rapid than dialysis. and permits the colloidal particles of different size present in a sol to be separated from each other if ultrafilters of different pore size are employed. The soluble impurities pass out in the filtrate while colloidal particles are retained by the filter paper in the form of slime. The slime is removed and resuspended in water to get the sol.

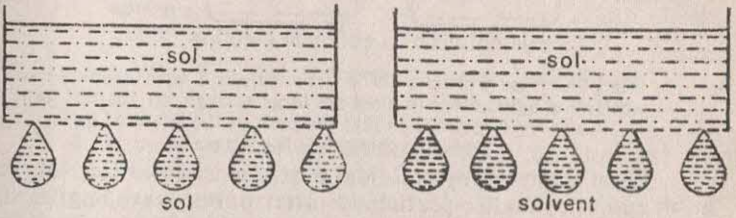

Fig. 4-5 (left). In filtration, colloidal particles pass through, so that they are not separated from the electrolytes present; the filtrate is the sol. itself (right). In ultrafiltration, the colloidal particles are held back while soluble impurities pass out in the filtrate; the filtrate is the pure solvent.

Lyophobic sols are sometimes stabilized by adding to them a small quantity of a lyophilic sol. Four example, gelatine, a lyophilic colloid, is added to ice-cream mix to produce a smoother product; gelatine prevents the colloidal particles of ice from coagulating and thus giving it a gritty structure. Gelatine is also added to milk to prevent curdling A protective colloid, such as glue, is added to electroplating baths to produce a smoother surface.

## 4. Properties of Colloidal Solutions

**1. Heterogeneity**. Colloidal solutions are heterogeneous systems consisting of the particles of a solid substance dispersed in a liquid. True solutions are homogeneous systems consisting of molecules or ions of the dissolved substance uniformly distributed in a liquid.

**2. Filtrability**. Colloidal particles are small enough so that they can easily pass through the pores of ordinary filter paper. However, they can be filtered out by using ultrafilters made of unglazed porcelain or of filter paper impregnated with collodion to reduce the size of its pores.

**3. Optical properties**. When a strong beam of light (*e.g.*, that from a projection lantern) is passed through an apparently transparent colloidal sol. the path of the beam becomes visible through the dispersion, if viewed in a darkened room (Fig. 4-6).

This phenomenon, called Tyndall's effect, arises from the fact that each colloidal particle scatters the light rays that fall upon it, becoming, in a sense, a luminous point. Particles of molecular or ionic size, as in true solutions, are too small to cause such a light scattering. Thus, Tyndall's effect is a means of readily differentiating a sol from a true solution.

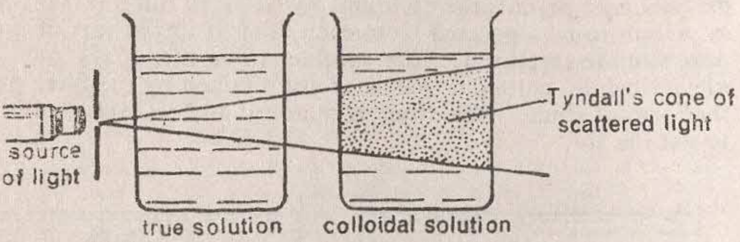

Fig. 4-6. The particles in a true solution are incapable of scattering light; those in a sol are large enough to scatter light in every direction, so that the path of the beam of light passing through is illuminated.

Light scattered by colloidal particles is also selectively scattered in colour. Smaller particles scatter shorter wavelengths of light; larger particles scatter longer wavelengths. Thus, silver sols of identical composition exhibit a wide variety of colours owing to the differing size of the dispersed particles (Table 4-3).

**Table 4-3.** *Colour of silver sols.*

| *Colour of silver sol.* | *Diameter of colloidal particle* |
|---|---|
| 1. Orange-yellow | $6 \times 10^{-5}$ mm |
| 2. Orange-red | $9 \times 10^{-5}$ mm |
| 3. Purple | $13 \times 10^{-5}$ mm |
| 4. Violet | $15 \times 10^{-5}$ mm |

For the same reason the sky at sunset appears to be dominated by orange and red colours. The light of setting sun passes through the lower layers of atmosphere, where larger particles scatter longer and still longer wavelengths of the solar spectrum.

The Tyndall effect is the underlying principle of the instrument called the ultramicroscope. An ultramicroscope differs from an ordinary one in this that in the former the light enters the liquid under study laterally, instead of from below. The arrangement of an ultramicroscope is shown diagrammatically in Fig. 4-7. An intense beam of light is sent through the liquid under study in a darkened space which is viewed under a powerful microscope directed at right angles to the beam. If the liquid is perfectly homogeneous (as a true solution is), all the fields of vision will appear dark as no light rays enter the tube of the microscope. If the liquid contains dispersed colloidal particles, the light scattered by them reaches the observer's eye making the particles appear as specks of bright light against a dark background. It may, however, be stressed again that the actual particles are not visible, but only the light scattered by them.

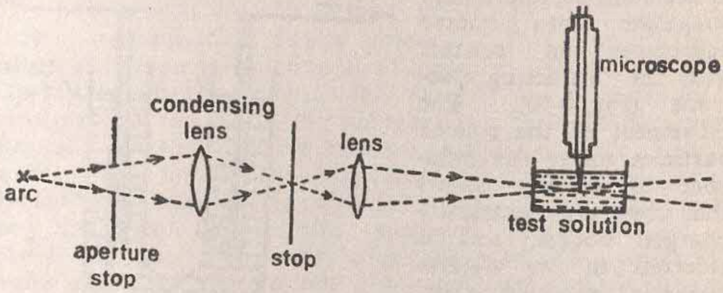

Fig. 4-7. The arrangement of an ultramicroscope.

**4. Kinetic properties** When colloidal particles are observed under an ultramicroscope, they are found to be in continual, rapid, and irregular motion in all directions (Fig. 4-8). This motion is caused by the continuous irregular bombardment of the dispersed particles by the molecules of the dispersion medium, and is called *Brownian movement* after the botanist Robert Brown who first observed it in 1828. The Brownian movement is an impressive evidence in support of the kinetic—molecular theory of matter. It must be realized, however, that molecular collisions are experienced by all particles dispersed in a medium whatever their dimensions. However, the motion acquired by the particles as a result of such collisions is discernable only when they are of colloidal size. When the particles are larger, the molecular collisions cause little movement because of the very large mass of the particles relative to the colliding molecules.

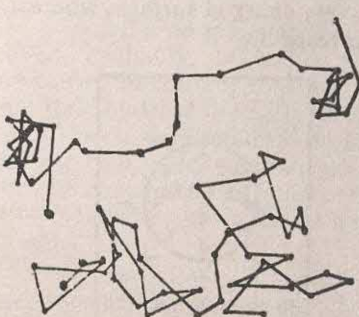

Fig. 4-8. Brownian movement of colloidal particles in a sol.

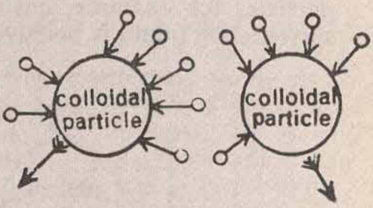

Fig. 4-9. Brownian movement is caused by the impact of molecules of dispersion medium; the thick winged arrows show the resultant of all such impacts and the direction in which the colloidal particle moves (large circles indicate collodal particles; small circles represent molecules of the dispersion medium).

**5. Electric charge**. When a lyophobic sol, *e.g.*, iron (III) hydroxide sol, is placed in an electrolytic cell, its colloidal particles move towards the anode or the cathode, and finally coagulate into coarse aggregates on contact with the attracting electrode (Fig. 4-10). The movement of the colloid particles under the influence of current shows that they are electrically charged bodies, and is referred to as *electrophoresis* (meaning electrical transfer of particles). All particles in any one colloidal system have the same charge. The colloidal particles of metal hydroxides are positively charged; particles of metals, sulphur and sulphides of metals have negative charges.

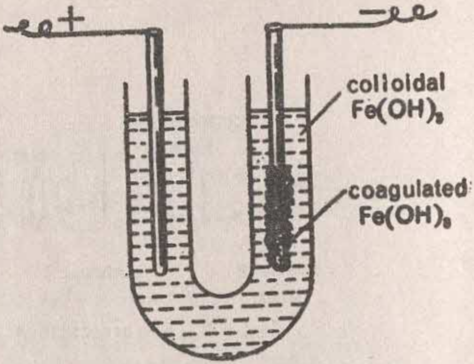

Fig. 4-10. Coagulation of iron (III) hydroxide sol in an electrolytic cell.

The colloidal particles develop electric charge by the adsorption of ions which exist in the surrounding solution If the colloidal particles adsorb predominantly or exclusively positive ions, they acquire positive charge. Thus the colloidal particles of iron (III) hydroxide formed by the hydrolysis of $FeCl_3$ in hot water preferentially adsorb iron (III) ions and become positively charged, leaving an excess of free hydroxyl ions in the solution. Arsenic (III) sulphide, $As_2S_3$, particles formed by the action of hydrogen sulphide on a solution of $As_2O_3$, adsorb $S^{2-}$ ions resulting from the ionization of $H_2S$ ($H_2S \rightleftharpoons 2H^+ + S^{2-}$), and acquire a negative charge. In the sol, the charged colloidal particles are surrounded by ions of opposite charge, called *counter ions* An arsenic (III) sulphide particle, for example, has negatively charged surface, whereas the surrounding liquid is positive with respect to it.

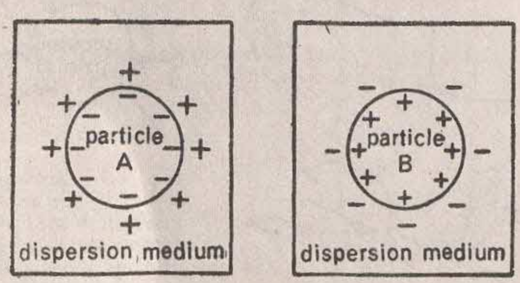

Fig. 4-11. Charges on colloidal particles. Particle A is negatively charged, and is surrounded by postiive ions in the dispersion medium; Particle B is positively charged, and is surrounded by negative counter ions in the dispersion medium.

**6. Precipitation or Coagulation.** Since all colloidal particles in a sol carry the same charge, they repel each other, thus tending to remain scatterd or suspended throughout the liquid. If by some means the charge on the colloidal particles is destroyed, th ey will approach each other and cluster into larger aggregates, so that a precipitate is finally produced. This is what happens when an electrolyte is added to a colloidal sol. The charged colloidal particles adsorb the oppositely charged ions produced by the electrolyte. In this way, the charge on the colloidal particles is neutralized, and the resulting neutral particles coalesce to form a precipitate. For instance when hydrochloric acid or sodium chloride is added to arsenic (III) sulphide sol, coagulation begins immediately, and arsenic (III) sulphide separates out of the liquid as a yellow precipitate. *The coagulating power of an ion, which is of opposite electrical sign to that of the colloidal particle, increases with increasing valency of the ion.* This statement is known as the **Hardy—Schulze rule.** Thus, for the precipitation of negatively charged arsenic (III) sulphide sol, divalent cations (*e g* , $Mg^{2+}$) are about 100 times, and trivalent cations (*e.g.*, $Al^{3+}$) about 700 times as effective as the monovalent cations (*e.g.*, $Na^{+}$). The rapid coagulation of blood, a typical colloidal dispersion, by alum (which furnishes the trivalent positive ion, $Al^{3+}$) illustrates the strong precipitation power of the trivalent ion. The use of alum in the purification of drinking water also depends upon the strong power of the $Al^{3+}$ ions to coagulate negative colloidal particles contained in large quantities in any natural waters.

Coagulation of colloidal particles in a sol is brought about not only by electolytes but also by other colloids with opposite charge on their particles. For example, when iron (III) hydroxide sol and arsenic (III) sulphide sol are mixed together, the dispersed particles of both sols coagulate, and a precipitate immediately appears. This precipitation is not caused by any chemical reaction between the two substances but by the neutralization of the charge on the particles of one by those of the other.

Coagulation of lyophobic sols also occurs when they are boiled. Probably, at higher temperatures the colloidal particles are caused to colloide together more frequently and vigorously so that they coalesce to finally form a precipitate. This is why colloidal dispersions produced during chemical analysis are boiled; boiling causes coagulation of the dispersed particles which can then be removed by filtration. Egg albumin, a hydrophilic colloid, is coagulated by hot water or hot grease in the poaching or frying of eggs.

Summing up, hydrophobic colloids can be precipitated by (1) electrolysis (*i.e.*, electrophoresis), (2) addition of electrolytes, (3) addition of oppositely charged sol, and (4) boiling. Hydrophilic colloids are more stable against coagulation.

7. **Adsorption.** Solid substances have a specific ability of attracting and holding other substances, *e.g.*, molecules of a gas or

molecules and ions of dissolved substances on their surface. This phenomenon, called *adsorption*, is apparently an electrical effect due to unbalanced electronic forces on the surface. Whereas the atoms, molecules, or ions at the surface in the interior of the body are surrounded on all sides by similar particles having equal attractive forces, those at the surface are surrounded by like particles only on one side. The surface particles, therefore, have unsatisfied attractive forces (Fig. 4-12). These unsatisfied forces, also called *residual valence forces*, are largely responsible for adsorption.

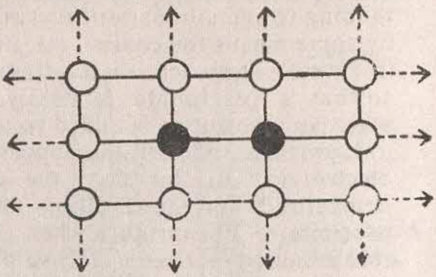

Fig. 4-12. Unsatisfied attractive forces (represented by dotted arrows) on surface particles (represented by unshaded circles).

Colloidal particles possess tremendous power of adsorption because they have a very large surface area for a given mass of material. The large surface area of colloidal particles is the result of the subdivision of material; the surface area of a material being a function of its particle size. Consider a solid cube 1 cm on each edge. If it is divided across the middle of each face, eight smaller cubes are formed, each 0·5 cm on each edge. The total surface area of the eight smaller cubes is $8[6 \times 0{\cdot}5 \times 0{\cdot}5]$ cm$^2$ or 12 cm$^2$. If the cube is divided into 1000 cubes each 0·1 cm on each edge, the total surface area becomes $1000[6 \times 0{\cdot}1 \times 0{\cdot}1]$ or 60 cm$^2$. If the subdivision is continued until cubes of colloidal dimensions, say $10^{-6}$, cm on each edge, are produced, the total number of particles will be $10^{18}$ and the total surface area $10^{18}[6 \times 10^{-6} \times 10^{-6}]$cm$^2$ or 6,000,000 cm$^2$. Because of their tremendous surface exposed to the surrounding medium, colloidal particles are powerful adsorbers. One volume of finely divided palladium adsorbs nearly 1000 volumes of hydrogen. It may also be recalled that lyophobic colloids are stabilized by adsorption of ions from the surrounding solution.

The term adsorption must be clearly distinguished from 'absorption'. Adsorption involves concentration of a substance on a surface; absorption involves its penetration into the bulk of the solid (Fig. 4-13). For example, moisture is adsorbed on a glass surface but absorbed in anhydrous calcium chloride.

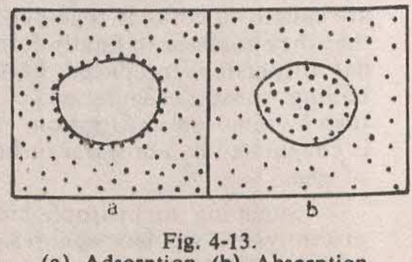

Fig. 4-13.
(a) Adsorption, (b) Absorption.

**8. Protection.** Hydrophobic sols are stabilized in the presence of a small quantity of a hydrophilic sol so that the coagulation does not occur so readily on addition of an electrolyte. Thus, if a little gelatine is added to a gold sol it is no longer coagulated by sodium chloride. The effect of a hydrophilic sol of making a hydrophobic sol much less susceptible to coagulation by electrolytes is called *protection* and the hydrophilic sol added for this effect is called a *protective colloid*. Gelatine, gum arabic, and dextrin are the most familiar and widely used protective colloids. The colloidal dispersion of silver halides used in the preparation of photographic films is stabilized by the addition of gelatine. Gum arabic is used in the stabilization of certain inks.

The mechanism of colloid protection can be explained in terms of adsorption. The lyophobic colloid absorbs the lyophilic colloid so that the latter forms a film surrounding each lyophobic colloid particle (Fig. 4-14). This film prevents interaction with the ions of the electrolyte and the consequent formation of clusters.

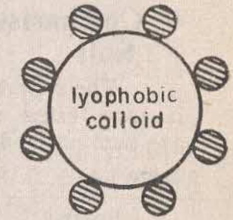

Fig. 4-14. Protective action of a lyophilic colloid (shaded circles) on a lyophobic colloid.

The protective action of lyophilic sols is compared in terms of the *gold number*. Gold number is the least number of milligrams of the protective colloid which must be added to prevent the coagulation (accompanied by a change in colour from red to blue) of 10 cm$^3$ of a standard gold sol on the addition of a 10 per cent aqueous solution of sodium chloride. The gold numbers of a few protective colloids are given below :

| | | | |
|---|---|---|---|
| Gelatine......... | 0·005 | Gum arabic......... | 0·15 |
| Egg albumin... | 0·08 | Gum tragacanth... | 2·0 |

Obviously, gelatine is the most effective one among these four protective colloids.

**Experiment 4.** Pour some dilute hydrochloric acid into two test tubes and add a little gelatine solution to one of them. Now add a few drops of silver nitrate solution to each test tube, and shake them well. A curdy precipitate of silver chloride is formed in the test tube not containing gelatine; in the other test tube, the entire liquid becomes turbid, but no precipitate separates.

## 5. Stability of Colloidal Sols

Colloidal particles are much larger than molecules and ions, and often more dense than the medium in which they are dispersed. Yet, they do not settle out from a sol, separated by the pull of gravity. There are at least three good reasons for the stability of colloidal sols.

1. *Brownian movement*. The colloidal particles in a sol, like the molecules or ions in a solution, are in a state of continuous rapid motion. Although the intensity of this motion, called Brownian movement, falls rapidly with increase in particle size, it is still high enough in the case of colloidal particles to offset the effect of gravity.

2. *Electric charge*. The colloidal particles in any sol are either all positively or all negatively charged. Particles bearing like charges, even upon close approach, will not collide and

coalesce, but will repel one another. Due to mutual repulsion, the colloidal particles tend to remain scattered or suspended throughout the liquid.

3. *Solvation.* The charged particles and their counter ions (see p. 124) are often highly hydrated in solution. The resulting hydrated 'shell' prevents close contact and cohesion of colloidal particles. This factor is particularly important in the case of hydrophilic colloids which are extensively hydrated in a sol.

As has been pointed out earlier, hydrophobic colloids are further stabilized by the addition of small amounts of a lyophilic colloid (protective colloid).

## 6. Comparison of Hydrophobic and Hydrophilic Sols

The difference between hydrophobic and hydrophilic colloids is manifested in many respects. The various points in this regard are summarized in Table 4-4.

**Table 4-4.** *A Comparison of hydrophobic and hydrophilic sols*

| *Property* | *Hydrophobic sols* | *Hydrophilic sols* |
|---|---|---|
| 1. Detection of particles | The particles may be readily detected by means of an ultramicroscope. | The particles are not readily detected by means of an ultramicroscope. |
| 2. Viscosity | Hardly differs from that of the dispersion medium. | Much higher than that of the dispersion medium. |
| 3. Electric charge | All particles in a sol have the same charge resulting from the adsorption of ions from the solution. | The charge on colloidal particles depends upon the *p*H of the medium, since the particles readily adsorb $H^+$ or $OH^-$ ions. This charge is often due to the dissociation of the molecules of the dispersed substance. |
| 4. Migration of particles in electric field | The particles migrate in one characteristic direction depending on the charge they bear. | The particles may migrate in either direction or not migrate at all, depending on the pH of the medium.* |
| 5. Stability (precipitation) | Dispersed particles are precipitated by the addition of small amounts of an electrolyte. | Dispersed particles are not precipitated by small amounts of electrolytes, although large quantities of electrolytes cause precipitation. |
| 6. Reversible/irreversible nature | When the liquid is removed, the resulting solid does not form sol again by the simple addition of the liquid. | When the liquid is removed, the resulting jelly-like solid (gel) is reconverted into sol by the addition of the liquid. |
| 7. Occurrence | Generally, do not occur naturally. | Most of these occur naturally. |

*At a certain *p*H the particles bear no net charge and, therefore, do not migrate in an electric field. This *p*H, called the *isoelectric point*, is different for different hydrophilic colloids.

**6-1. Relative stability of hydrophobic and hydrophilic sols.** Hydrophobic sols are coagulated by the addition of small quantities of electrolytes, just sufficient to neutralize the charge on them. Hydrophilic colloids, on the other hand, require the addition of much larger quantities of electrolytes for coagulation to occur. The reason is that hydrophilic colloids are extensively hydrated and are surrounded by a dense shell of water molecules (the hydrate shell). This shell keeps them from clustering even when the charge on the particles has been removed by the electrolyte. Thus, in the case of hydrophilic colloids mere removal of the charge on the particles is not enough, the hydrate shells, too, have to be destroyed before coagulation can occur. This necessitates the addition of electrolytes in large quantities. The ions from the extra electrolyte take away the water molecules of the hydrate shells of colloid particles, and become themselves hydrated. This causes the coagulation of the sol. The coagulation of lyophilic sols by electrolytes is usually called *salting out*. A familiar example of the coagulation of a lyophilic colloid by the addition of electrolyte is the 'salting out' of soap by adding sodium chloride to the suspension.

In general, the main stability factor for lyophobic sols is the charge on their particles, while solvation of the dispersed particles is the main stability factor for lyophilic sols. A lyophobic sol is coagulated when the charge on its particles is removed; a lyophilic sol is coagulated when the charge as well the hydrate shell of the particles are removed. This is illustrated diagrammatically in Fig. 4-15.

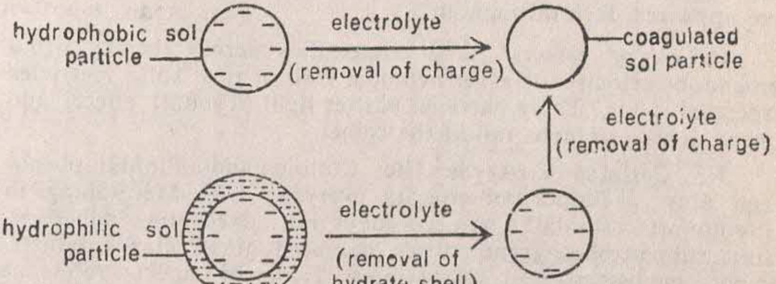

Fig. 4-15. Coagulation of sols by electrolytes; much more quantity of electrolyte is required for the coagulation of lyophilic sols as the electrolyte is used up not only for the removal of charge on the particles, but also of their hydrate shells.

## 7. Some Practical Aspects of Colloids

**7-1. Colloids in life processes.** Most of the components of living organisms such as blood and other body fluids, muscle tissue, bone, skin, and hair involve colloidal materials. Included also are the ***biocatalysts*** : enzymes, hormones, and vitamins. Salts dissolved in the watery fluids of the body are the electrolytes which control the dispersion of various colloidal systems in the body.

Any imbalance in the degree of dispersion of the colloidal proteins in the organs and tissues of the body is manifested in certain mental disorders and swelling of the tissues. Almost all foods and their components such as starches (insoluble carbohydrates), proteins, and fats are colloidal materials. The whole process of assimilation of food is one of colloidal chemistry.

**7-2. Colloids in nature.** Many natural phenomena are based on the colloidal properties of substances.

1. *Formation of deltas.* Colloidal clay or silt particles in a river are negatively charged by the preferential adsorption of hydroxide, $OH^-$, ions. When the river water strikes the salty ocean water, two things happen : (1) The less dense river water fans out over the denser sea water in a surface layer, and (2) the negatively charged clay and silt particles which are stable in river water have their charges cancelled by the ions (*e.g.*, $Na^+$ and $Mg^{2+}$) in the sea water, and are thereby precipitated. The deposition of the precipitated clay and silt during thousands of years produces a fan-shaped delta at the mouth of large rivers.

2. *Soil.* Soil consists of colloidal particles which can adsorb moisture and nourishing materials. Fertile soils contain humus (decayed animal and vegetable material) which acts as the protective colloid.

3. *Blue colour of sky.* The colloidal dust particles floating about in the sky scatter blue light, thus making the sky appear blue. In the absence of these colloidal particles the sky would have appeared dark throughout.

4. *Tail of comets.* As a comet flies across the sky with a tremendous velocity, it leaves behind a trail of tiny solid particles suspended in air. These particles scatter light (Tyndall effect) and appear as the luminous tail of the comet.

**7-3. Colloids in everyday life.** Colloids and colloidal phenomena play an important role in everyday life. Many things in daily use are colloidal in nature—soaps, inks, dyes, glues, adhesives, paints, rubber, photographic films, coloured glass, clay products, cement, medicines, and many more. However, special reference may be made in respect of the following :

1. *Medicines.* Colloidal medicines are readily adsorbed in the system and are, therefore, more effective. Colloidal gold, colloidal calcium etc. are administered by intravenous injection to increase vitality. Argyro. and protargol are protected colloidal solutions of silver (argentum) used in the treatment of granulations in eyes.

2. *Purification of water.* The purification of drinking water involves the coagulation of suspended colloidal particles of clay, sand, etc. by the addition of alum. The alum, being a salt of aluminium, furnishes in water solution tripositive aluminium ions, $Al^{3+}$. These ions discharge the negatively charged dirt or clay

particles suspended in water, causing them to coagulate. Furthermore, the aluminium sulphate in alum* is partly hydrolyzed by water to produce colloidal aluminium hydroxide which adsorbs suspended particles.

3. *Curdling of milk*. The fermentation of the sugar in the milk produces lactic acid. The electrically charged ions from the acid cause the colloidal particles in the milk to discharge, coalesce, and separate as curd. The same effect is produced when any other acid is added to the milk.

4. *Cooking of foods*. Poaching and frying of egg involve the coagulation of egg albumin, a lyophilic colloid, by hot water and hot grease respectively. The cooking of rice, potato, etc. involves the coagulation of starch particles.

**7-4. Colloids in technology**. Many colloidal phenomena have important technological applications. Some of these are :

1. *Smoke precipitation*. The smoke and dust particles from furnaces are charged colloids. These are removed by using a device, called Cottrel precipitator, after the name of the inventor, Dr. Frederic G. Cottrell, an American chemist. In this device (Fig. 4-16) the charged particles suspended in the smoke are attracted to highly charged electrodes, where they lose their charge, coagulate, and drop down as dust. Dust-free gases escape from the stack.

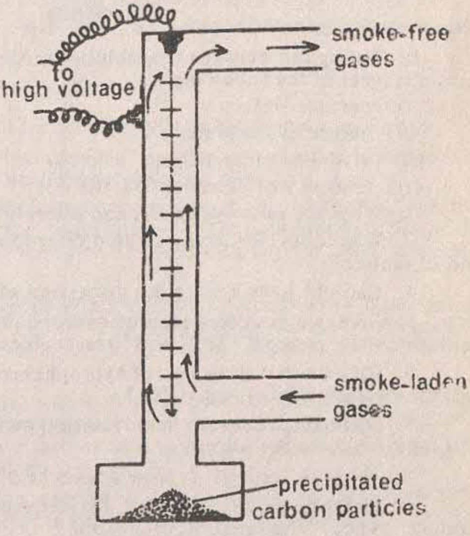

Fig. 4-16. Smoke precipitation in Cottrel precipitator.

The precipitated dusts from smelters, furnaces, and kilns often contain valuable by-products which, in the absence of electric precipitator, would have literally gone up in smoke. Potassium salts are recovered from the dust of cement kilns while arsenic (III) sulphide is recovered from the dust of furnaces and smelters in which metal sulphides are roasted.

2. *Rubber precipitation*. The sap of rubber tree, called *latex*, is a milky liquid consisting of negatively charged rubber particles. These are coagulated by the addition of acetic acid.

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*Alum is the double sulphate of potassium and aluminium corresponding to the formula $K_2SO_4.Al_2(SO_4)_3.24H_2O$.

3. *Sewage disposal*. Dirt particles suspended in water are mostly negatively charged colloids. These are removed by allowing the dirty water to flow through big sewage disposal tanks fitted with metallic electrodes (Fig. 4-17). The colloidal dirt particles lose their charge at the oppositely charged electrodes, coagulate, and settle down as sludge. The sludge is used as manure and the clear water is used for irrigation.

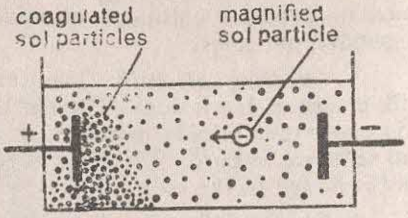

Fig. 4-17. Sewage disposal.

4. *Dyeing*. In the dyeing of cotton fabrics, the cloth is first treated with a colloidal suspension of a substance, called ***mordant*** (*e.g.*, aluminium hydroxide). The colloid has a strong adsorptive attraction for the fabric on one hand and for the dye on the other. As a result, the dye sticks fast to the fabric for the length of its life.

## Questions

1. Distinguish between true solutions, colloidal solutions, and suspensions in respect of the following :

(*i*) particle size,

(*ii*) nature of the system,

(*iii*) visibility of particles,

(*iv*) tendency of particles to settle out.

2. What are *sols, hydrosols*, and *alcosols* ?

3. Why does the term colloid refer to a 'state' of matter rather than a kind of matter ?

4. Can one have a colloidal dispersion of a gas in a gas ? Explain.

5. Give two examples each of hydrophobic and hydrophilic sols. Why are these called 'reversible sols' and 'irreversible sols' respectively ?

6. How do the viscosities of hydrophobic and hydrophilic sols compare with the viscosity of distilled water ?

7. Distinguish between 'condensation methods' and 'dispersion methods' for preparing colloidal solutions.

8. What is 'dialysis' ? How does it help the colloidal sol to stabilize ?

9. Gelatine is often added to ice-cream mix to produce a smoother product. What is the function of gelatine ?

10. The path of a strong beam of light becomes visible through a colloidal sol but not through a true solution. Explain the reason. What is this effect called ?

11. What is Brownian movement ? How does it originate ?

12. What is electrophoresis ? In what respects does it differ from electrolysis ?

13. Explain the difference between the electric charge on ions and on colloidal particles.

14. State four methods for coagulating hydrophobic colloidal dispersions.

15. State *Hardy-Schulze rule*. Arrange the electrolytes $Na_2SO_4$, $MgSO_4$, and $Al_2(SO_4)_3$ in the increasing order of their effectiveness in coagulating the negatively charged arsenic (III) sulphide sol.

16. Why should $MgSO_4$ be more effective in coagulating a $Fe(OH)_3$ dispersion in water than NaCl ?

17. Distinguish between 'adsorption' and 'absorption' with a suitable example.

18. Define 'gold number'. Name any two protective colloids.

19. Explain the protective action of a hydrophilic colloid upon a hydrophobic sol.

20. Why do the heavy particles of colloidal gold not sink in water ?

21. A much more quantity of electrolyte is required for the coagulation of a hydrophilic sol than that for the coagulation of a hydrophobic sol. Explain the reason.

22. The suspended particles carried by rivers are partially of colloidal size. How does this fact explain the formation of river deltas where the rivers flow into the ocean ?

23. How would you account for the following :

(*a*) Blue colour of sky,

(*b*) Tail of comets,

(*c*) Curdling of milk on long standing,

(*d*) The use of potash alum in the purification of water.

24. Discuss the principle of smoke precipitation.

25. Why is the cotton cloth required to be mordanted before dyeing ? Explain.

## Key

12. Electrophoresis differs from electrolysis in the following respects :

(*i*) Electrolysis involves the chemical decomposition of the electrolyte; electrophoresis does not involve chemical decomposition.

(*ii*) The products of electrolysis appear on both electrodes, electrophoresis results in the coagulation of the colloidal particles of the sol on either of the two electrodes depending on the charge on the colloidal particles.

13. The electric charge on ions arises by transfer of electrons from or to neutral atoms (positive charge by the loss and negative charge by the gain of electrons); that on colloidal particles arises by the adsorption of ions which exist in the surrounding solution.

16. $Fe(OH)_3$ dispersion in water is positively charged; hence it will be coagulated by negative ions. The negative ions furnished by $MgSO_4(SO_4^{2-})$ being divalent are more effective in coagulating $Fe(OH)_3$ than those furnished by NaCl ($Cl^-$) which are monovalent.

20. Owing to (*i*) Brownian movement of the colloidol particles which offsets the effect of gravity, and (*ii*) the negative charge on all gold particles so that they repel each other and remain scattered throughout the liquid.

□

## 5

# Electrode Potentials

The chemical activity of metals was originally described in terms of their ability to 'displace' hydrogen from acids. On this basis metals were arranged in a series, called the activity series, in which hydrogen was included as a sort of dividing line between those metals which are more active and those which are less so. Any metal above hydrogen in this series will displace hydrogen gas from acids and will displace a lower metal from a solution of its ions.

Today, the activity of metals is described in terms of their ability to lose electrons measured as their standard electrode potentials. The activity series, now called *electrochemical series*, is the arrangement of elements in order of decreasing standard potentials; the smaller the value of the potential, the weaker the tendency for a metal to ionize *i.e.*, to lose electrons, and vice versa.

## 1. Meaning of the Electrode Potential

When a piece of metal is placed in a solution containing its ions, some of its atoms tend to give up electrons to the piece of metal and go into solution as positive ions. The accumulation of electrons on the metal surface builds up an electrostatic field which tends to hold the positive metal ions close to the metal surface. At the same time, however, some of the metal ions already in solution tend to take up electrons from the metal and deposit themselves as neutral atoms. Whichever tendency is greater in a given case determines whether the metal will become negatively charged or positively charged with respect to the solution. A rod of zinc, for example, becomes negatively charged owing to the net ionization of some of its atoms. As a result, it attracts a layer of positive $Zn^{2+}$ (*aq*) ions to form an electrical double layer* (Fig. 5-1.) When equilibrium is eventually established, the two opposing processes continue at the same rate without any change in the potential difference. The charge build up on the metal is minute and an equilibrium involving zinc atoms, excess electrons on the

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*This can be compared to an electric capacitor, one plate being the charged metal surface, and the other the layer of ions near it.

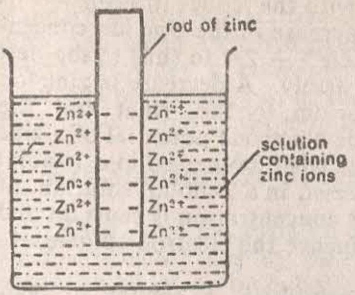

Fig. 5-1. Electrical double layer at the surface of zinc metal in a solution containing zinc ions, $Zn^{2+}$.

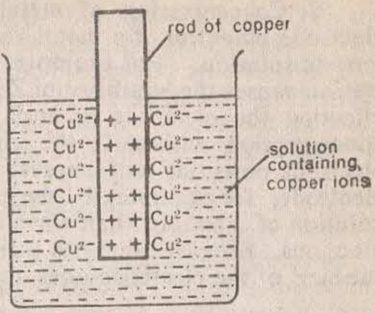

Fig. 5-2. Electrical double layer at the surface of copper metal in a solution containing copper ions, $Cu^{2+}$.

piece of zinc metal, and adsorbed $Zn^{2+}(aq)$ ions quickly develops. This can be represented as

$$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$$

In the case of less active metals, like copper, the tendency of the positive metal ions to pick up electrons from the metal atoms predominates over the tendency of metal atoms to lose electrons and go into solution as positive ions. Consequently, the metal becomes positively charged with respect to the solution. In this case, too, an electrical double laycr is formed as shown in Fig 5-2.

There is an electrical potential difference across the double layer at a metal surface, due to the separation of charges. *The potential difference between a metal and a solution of its ions (in equilibrium) is known as the electrode potential of the metal.* The electrode potential of metal serves as a measure of its capacity for yielding electrons and, therefore, of its chemical activity during reactions taking place in solution.

## 2. Factors Affecting Electrode Potentials

At equilibrium the potential difference between the metal and the solution of its ions, *i.e.*, the electrode potential is dependent upon the following factors :

1. **Nature of the metal.** Since no two metals (conductors) have the same electron structures, no two metals can have exactly the same tendency to lose electrons, *i.e.*, the same electrode potential. The more active the metal the greater is the tendency to form ions and the more negative is the potential of the electrode with respect to the solution. Thus, zinc being more active than copper, has stronger tendency to lose its electrons; that is, it has a higher electrode potential.

2. **Concentration of metal ions in solution**. The size of the electrode potential of a metal varies with the concentration of its ions in solution. For example, an increase in the zinc ion concentration causes the equilibrium $Zn \rightleftharpoons Zn^{2+} + 2e^-$ to shift to the left affecting the electrode potential adversely. A decrease in zinc ion concentration will shift the equilibrium to the right and the electrode potential will increase. The electrode potential of a zinc electrode, for example, will be greater when immersed in a 1-molal solution of zinc ions than when immersed in a 2-molal solution of zinc ions. Because zinc is a solid, its concentration is constant and the size of the electrode does not influence the electrode potential.

3. **Temperature**. As with most equilibria, a change in temperature will cause a shift in the equilibrium

*metal* $\rightleftharpoons$ *metal ions*.

shift towards one side or the other. Hence, the electrode potential of a given metal will vary with the temperature of the solution.

## 3. Standard Electrode Potentials

Since the electrode potential of a given metal varies with the concentration of its ions in solution and upon the temperature, it is necessary to specify both of these variables before comparing the values for different elements. The potential developed when an electrode is in contact with a molar solution of its ions at 25°C is arbitrarily chosen as the basis for comparison, and is known as the ***standard electrode potential*** of that element.

No satisfactory method has been devised for measuring single electrode potentials, *i.e.*, the absolute difference in electrical potential between a metal electrode and a solution of its ions. However, the difference between the potentials of two electrodes can be easily measured For the measurement of electrode potentials, a hydrogen electrode dipping into a solution containing hydrogen ions at a concentration of 1M at 25°C has been adopted as a standard for comparison. This is called ***standard hydrogen electrode*** and its potential has been arbitrarily assigned the value 0·000 *V*. ***The standard electrode potential of any given electrode***, then, ***is the difference of potentials (in volts) between its electrode potential when the concentration of the ion in the solution is 1M and that of a standard hydrogen electrode dipping into a solution of 1 M activity of*** $H^+$ ***ions, at 25°C.*** The standard electrode potentials determined against this standard are known as the standard electrode potentials on the ***hydrogen scale***. These are represented by the symbol $E°$. Thus, composed with the standard hydrogen electrode potential of 0.00 volt, the standard electrode potential of magnesium is +2.34 volts, that of zinc is +0.76 volt, and that of copper is −0.34 volt. The reason for designating the potentials of magnesium and zinc as positive and that of copper as negative is given in section 5, page 138.

It must be clearly understood that the potential of the standard hydrogen electrode is only arbitrarily taken as zero. This does not mean that hydrogen has no electrode potential at all. It simply provides a convenient basis of comparison for all other electrode potentials, just as the freezing point of water is conventionally accepted as the zero of temperature on the Celsius scale.

## 4. The Standard Hydrogen Electrode

How can a gas form an electrode ? For practical purposes, a solid conductor has to be employed. Single electrodes involving gases can be set up by bubbling the gas over an inert metallic conductor that will conduct electrons but will not itself take part in the electrode reaction. Thus, the standard hydrogen electrode is constructed as follows. A piece of platinum foil is coated electrolytically with finely-divided platinum (called platinum black) to give it a large surface area. It is then suspended in a solution containing hydrogen ions at a concentration of 1M, and surrounded by a glass jacket. Pure hydroen gas . at a pressure of 1 atm, is continually bubbled over the platinized platinum electrode (Fig. 5-3). Hydrogen is adsorbed and the electrode, in effect, presents a surface of hydrogen to the solution and acts as a 'metallic' hydrogen electrode. Activation of the hydrogen by platinum results in a tendency of its atoms to ionise and lose electrons to the platinum, making it negative. This tendency is opposed by that of the H+ ions in

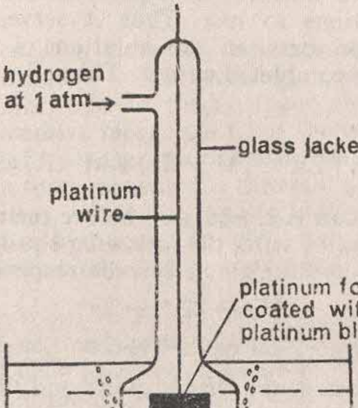

Fig. 5-3. The hydrogen electrode.

solution to acquire electrons from the negatively charged platinum and be reduced to hydrogen. A difference in potential between the electrode and the solution is established as a consequence of the following equilibrium :

$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

It is thus obvious that the hydrogen electrode will have a certain potential. However, this potential is arbitrarily assigned the value zero. The need for bubbling hydrogen under a specified pressure arises from the fact that with hydrogen (and any other gas) electrode, the potential will vary directly with the partial pressure of the gas.

## 5. Measurement of Standard Electrode Potentials

The electrode potentials are measured with the aid of voltaic cells in which one of the electrodes is the metal under test, and the other, a hydrogen electrode, hooked up through a voltmeter. For example, the standard electrode potential of zinc is measured by setting up an electrochemical cell consisting of a zinc electrode dipping into a 1M solution of zinc ions as one half of the cell and a standard hydrogen electrode as the other half (Fig. 5·4). The two halves of the cell are connected by a salt bridge consisting of a saturated solution of potassium chloride in a gel of agar-agar. This bridge permits ions to move freely through it but does not allow the two solutions to mix. Thus it serves to establish an electrical connection between the solutions of the two electrodes and thereby make a completed circuit. The cell notation is

$$\text{Zn} \mid \text{Zn}^{2+}, \text{1M} \overset{\overset{e^-}{\rightarrow}}{\|} \text{H}^+, \text{1 M} \mid \text{H}_2\,(\text{Pt}), \text{1 atm}$$

Before the circuit is closed, *i.e.*, before the zinc and platinum strips are connected by wire, the following equilibria obtain at the hydrogen electrode and the zinc electrode respectively.

$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

$$Zn \rightleftharpoons Zn^{2+} + 2e^-$$

Upon closing the circuit, the current flows and the zinc is found to dissolve. This shows that the equilibrium at the zinc electrode is shifted to the right causing more zinc atoms to lose electrons and be oxidized to zinc ions.

$$Zn \rightarrow Zn^{2+} + 2e^-$$

The electrons lost by zinc flow to the hydrogen electrode through the connecting wire. As a result of the inflow of electrons, the equilibrium at the hydrogen electrode is shifted to the left causing hydrogen ions to be reduced to free hydrogen.

$$2H^+ + 2e^- \rightarrow H_2$$

Zinc, where oxidation (loss of electrons) occurs is the anode; hydrogen, where reduction (gain of electrons) occurs is the cathode. The reactions that take place at the electrodes when the zinc-hydrogen cell is operating are :

(anodic oxidation) : $Zn \rightarrow Zn^{2+} + 2e^-$

(cathodic oxidation) : $2H^+ + 2e^- \rightarrow H_2$

(over-all reaction) : $Zn + 2H^+ \rightarrow Zn^{2+} + H_2\uparrow$

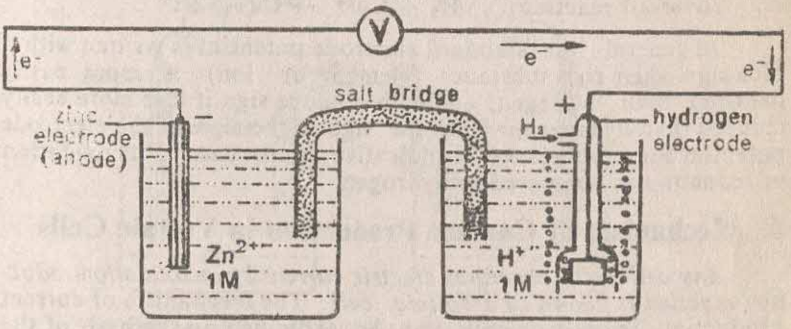

Fig. 15-4. Measurement of the electrode potential of zinc.

The difference in potential between the two half cells as measured by a voltmeter is the force that causes electrons to move from the zinc electrode to the hydrogen electrode. This force is called the **electromotive force (e.m.f.)** of the cell and is 0·76 volt. As the potential of hydrogen electrode is assumed to be 0·000 volt, the electromotive force measured is the standard electrode potential of zinc. It is written with a plus sign to indicate that zinc is more easily oxidized than hydrogen, or, zinc has the higher electrode potential. The standard electrode potential of zinc is, therefore, +0·76 volt.*

In a voltaic cell consisting of a copper electrode dipping into a 1M solution of $Cu^{2+}$ ions and a standard hydrogen electrode, the electrons flow from the hydrogen electrode to the copper electrode where they reduce $Cu^{2+}$ ions to neutral atoms. Obviously, copper has a lower electrode potential than hydrogen; or, hydrogen has a greater tendency to form positive ions and leave electrons than does copper. The standard electrode potential of copper is, therefore, given a negative value, —0·34 volt; the E.M.F. of the cell

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*It must be understood that the electrode potential 0·76 volt for the half-reaction $Zn \rightarrow Zn^{2+} + 2e^-$ is, in fact, the oxidation potential. If it is written as the reduction potential, the reaction would be reverse, and the sign would be opposite. Thus, for the reduction half-reaction $Zn^{2+} + 2e^- \rightarrow Zn$, the potential ($E^\circ$) is —0·76 volt. The same applies to all the electrode potentials given in Table 6-1, page 141

$$\overset{\overset{e^-}{\rightarrow}}{\mathrm{H_2\,(Pt),\ 1\ atm\ |\ H^+,\ 1\ M\ \|\ Cu^{2+},\ 1\ M\ |\ Cu}}$$

as measured by a voltmeter being 0·34 volt. The reactions taking place in a copper-hydrogen cell in operation are :

$$\begin{array}{ll} \text{(anodic oxidation)} & : \quad \mathrm{H_2 \rightarrow 2H^+ + 2}e^- \\ \text{(cathodic reduction)} & : \underline{\mathrm{Cu^{2+} + 2}e^- \rightarrow \mathrm{Cu} \qquad\qquad} \\ \text{(over-all reaction)} & : \mathrm{H_2 + Cu^{2+} \rightarrow Cu + 2H^+} \end{array}$$

In general, the standard electrode potential is written with a plus sign when the substance (element or ion) is more easily oxidized than hydrogen, and with a minus sign if it is more easily reduced than hydrogen. Thus the sign of the sign of the electrode potential for a substance is indicative of the case of its oxidation or reduction as compared to hydrogen.

## 6. Mechanism of Current Production in Voltaic Cells

*Any cell which generates electric current by an oxidation-reduction reaction is known as a voltaic cell.* The mechanism of current production in voltaic cells can be explained on the basis of the electron densities acquired by the two electrodes. Consider, for instance, a zinc-copper cell (Fig. 5-5). In this cell, the zinc electrode dipped in the zinc sulphate solution acquires a high current density as it has a strong tendency to pass into solution as the positive ions, $Zn^{2+}$. The copper electrode dipped in the copper sulphate solution, becomes electron deficient (*i.e.*, positively charged) as the $Cu^{2+}$ ions in the solution have a stronger tendency to take on electrons from the atoms of copper than the opposing tendency. If the electrodes are not connected to one another by a conductor, the following equilibria will be established :

$$\mathrm{Zn \rightleftharpoons Zn^{2+} + 2}e^- \text{ (at the zinc electrode)}$$
$$\mathrm{Cu \rightleftharpoons Cu^{2+} + 2}e^- \text{ (at the copper electrode)}$$

and there will be no further passage of zinc ions into the solution or the deposition of copper atoms from the solution containing $Cu^{2+}$ ions. Upon closing the electrical circuit, the electrons accumulating on the zinc start flowing through the wire connecting the two electrodes to the copper electrode where there is a shortage of electrons. As the electron density increases at the copper electrode, the equilibrium is shifted to the left, causing copper ions to be reduced to copper atoms.

$$\mathrm{Cu \leftarrow Cu^{2+} + 2}e^-$$

At the same time the electron density at the zinc electrode decreases, and the equilibrium at the zinc electrode is shifted to the right causing more zinc atoms to give up electrons and change into zinc ions :

$$Zn \rightarrow Zn^{2+} + 2e^-$$

Thus, the zinc is able to send more and more $Zn^{2+}$ ions into the solution, while $Cu^{2+}$ ions continue to be discharged at the copper electrode and to deposit as copper metal. The two processes continue until all the zinc is dissolved or the $Cu^{2+}$ ions are used up completely.

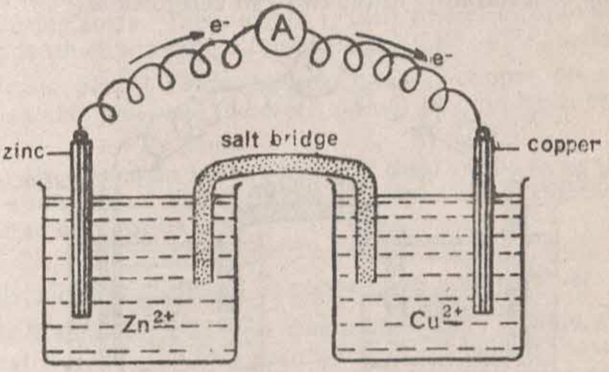

Fig. 5-5. A voltaic cell involving zinc and copper electrodes.

It will, however, be wrong to infer from the above description that in a voltaic cell, one of the electrodes must become negatively charged and the other positively. The only requirement for the flow of electrons from one charged body to another is that they should have different potentials or electron densities. This conditions is met whenever a galvanic cell is set up with two poles of *different electrode potentials*. The reason is that the capacity for splitting off electrons and passing into ions is different in different metals. In a galvanic cell consisting of zinc and iron dipping in 1M solutions of their salts, both metals will be negatively charged in their respective solutions. Yet, there will be a definite difference of potentials between them. If the metals are connected with a conducting wire, the current will be produced due to the flow of electrons from the zinc having a higher electrode potential to the iron having a lower electrode potential. The zinc will dissolve and the iron will deposit from solution containing $Fe^{2+}$ ions. The reactions taking place in the cell

$$\overset{e^-}{\rightarrow}$$

$$Zn \mid Zn^{2+}, 1M \parallel Fe^{2+}, 1M \mid Fe$$

can be represented by the equations given below :

(anodic oxidation) : $Zn \rightarrow Zn^{2+} + 2e^-$

(cathodic reduction) : $Fe^{2+} + 2e^- \rightarrow Fe$

(over-all reaction) : $Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$

Since the electrode potential of any given metal will vary with the concentration of the metal ions in solution, a voltaic cell may be constructed with half cells having tha same two electrodes but different concentrations of the common ion around them. Such a cell is called a *concentration cell*. In the concentration cell shown in Fig. 5-6 a continuous flow of electrons will occur from the zinc in the 1M zinc ion solution to the zinc in the 2M zinc ion solution since electrode potential of the former is somewhat greater than that of the latter (p. 134). This will continue so long as a difference in zinc ion concentration in the two half cell remains.

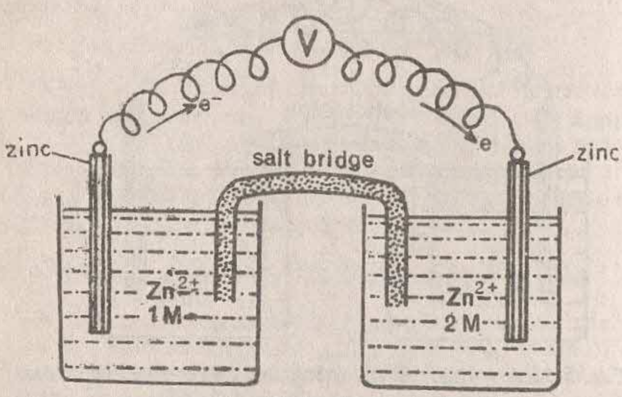

Fig. 5-6. A concentration cell.

While theoretically possible, concentration cells are not in common use, since the difference of potentials obtained is extremely small. The other type of voltaic cell in which two poles of different electrode potentials are used is more practical, and is the type of nearly all our modern cells.

## 7. The Electrochemical Series

When the elements are arranged in the order of their standard electrode potentials from the most positive to the most negative, we have the electrochemical series of elements (also called the *electromotive* series of elements). Table 5-1 (given on the next page) gives the electrochemical series for some of the elements. In this series each metal is less active than the one preceding it. The decreasing activity of the metals downward the series is due to the decreasing tendency of their atoms to lose electrons and exist as positive ions in solution. For example, iron has much stronger tendency to lose electrons than copper. Hence, iron passes into solution as positive ions more readily than does copper. That is, the reaction

$$Fe \rightarrow Fe^{2+} + 2e^-$$

occurs more readily and in preference over the reaction

$$Cu \rightarrow Cu^{2+} + 2e^-$$

Hence, (*i*) iron displaces hydrogen from acids while copper does not, and (*ii*) iron displaces copper from solutions of its salts while copper does not similarly displace iron.

In the electrochemical series—

(1) The electropositive character, chemical reactivity, and the reducing power of the elements progressively diminish downward. *Higher the standard electrode potential, stronger is the reducing agent.*

(2) All metals placed above hydrogen displace hydrogen from non-oxidizing acids. These metals readily lose electrons to $H^+$ ions from acids which are reduced to hydrogen ($2H^+ + 2e^- \rightarrow H_2$).

Metals placed below hydrogen, *e.g.*, copper do not lose electrons to $H^+$ ions and, therefore, do not liberate hydrogen from acids.

(3) Each element in the series will displace the elements below it from a solution of their salts. For example, zinc displaces copper from the solution of its salts.

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

Similarly, silver is displaced by copper, and gold by silver.

(4) Metals such as zinc, magnesium, and aluminium provide *sacrificial protection* to iron against corrosion. Being above iron in the series they dissolve preferentially on exposure, transferring electrons to the iron in contact. The ionization of iron is thus prevented so long any one of these metal exists in contact with it.

(5) The e.m.f. of any cell formed from two metal electrodes equals the algebraic difference between their electrode potentials. For the electromotive force to have a positive value, the smaller

**Table 5-1.** *Electrochemical series for some common elements*

| *Element* | *Electrode reaction* | | | *Electrode potential (volts)* |
|---|---|---|---|---|
| | *Reduced form* | | *Oxidized form* | |
| Potassium | K | ⇌ | $K^+ + e^-$ | + 2·92 |
| Calcium | Ca | ⇌ | $Ca^{2+} + 2e^-$ | + 2·76 |
| Sodium | Na | ⇌ | $Na^+ + e^-$ | + 2·71 |
| Magnesium | Mg | ⇌ | $Mg^{2+} + 2e^-$ | + 2·34 |
| Aluminium | Al | ⇌ | $Al^{3+} + 3e^-$ | + 1·67 |
| Zinc | Zn | ⇌ | $Zn^{2+} + 2e^-$ | + 0·76 |
| Iron | Fe | ⇌ | $Fe^{2+} + 2e^-$ | + 0·44 |
| Tin | Sn | ⇌ | $Sn^{2+} + 2e^-$ | + 0·14 |
| Lead | Pb | ⇌ | $Pb^{2+} + 2e^-$ | + 0·13 |
| Hydrogen | $H_2$ | ⇌ | $2H^+ + 2e^-$ | + 0·00 |
| Copper | Cu | ⇌ | $Cu^{2+} + 2e^-$ | — 0·34 |
| Silver | Ag | ⇌ | $Ag^+ + e^-$ | — 0·80 |
| Mercury | Hg | ⇌ | $Hg^{2+} + 2e^-$ | — 0·85 |
| Platinum | Pt | ⇌ | $Pt^{2+} + 2e^-$ | — 1·20 |
| Gold | Au | ⇌ | $Au^+ + e^-$ | — 1·68 |

potential is always subtracted from the larger. For instance, the e.m.f. of a Daniel cell consisting of copper and zinc electrodes in solutions of their respective ions is $+0{\cdot}76-(-0{\cdot}34)=1{\cdot}10$ volts.*

(6) The metals are discharged in the order of their electrode potentials during the electrolysis of aqueous solutions containing their ions. The metal with the lowest electrode potential will be discharged first since it has the weakest tendency to exist as ions in solution, and when all of its ions have been discharged as atoms, another metal higher up the series will begin to deposit. This selective discharge of ions is of great significance in the electrolytic refining of metals and in electroplating.

(7) Owing to their great reactivity, metals near the top of the series do not occur free in nature. Those near the bottom of the series often occur free in nature.

**7-1. Predicting reactions.** To predict if an oxidation-reduction reaction will take place or not, the two half-reactions are written and their potentials added. If the total potential, $E^\circ_T$, is positive, the reaction will go spontaneously; if it is negative, it will not (when $E^\circ_T$ values are positive by only a few hundredths of a volt, the reaction may not occur). Consider the following examples (all concentrations 1·00 M) :

1. $Mg + 2H^+ \rightarrow Mg^{2+} + H_2$ ?

Two half reactions are :

$$\begin{array}{ll} Mg \rightarrow Mg^{2+} + 2e^- & E_o = +2{\cdot}34 \text{ volt} \\ 2H^+ + 2e^- \rightarrow H_2 & E_o = 0{\cdot}0 \text{ volt} \\ \hline Mg + 2H^+ \rightarrow Mg^{2+} + H_2 & E^\circ_T = +2{\cdot}34 \text{ volt} \end{array}$$

$E_T$ being positive, the reaction will go spontaneously as written.

2. $Mg^{2+} + Zn \rightarrow Zn^{2+} + Mg$ ?

Two half reactions are :

$$\begin{array}{ll} Mg^{2+} + 2e^- \rightarrow Mg & E_o = -2{\cdot}34 \text{ volt} \\ Zn \rightarrow Zn^{2+} + 2e^- & E_o = +0{\cdot}76 \text{ volt} \\ \hline Mg^{2+} + Zn \rightarrow Zn^{2+} + Mg & E^\circ_T = -1{\cdot}58 \text{ volt} \end{array}$$

$E_T$ being negative, this reaction will not occur as written (the reverse reaction would since $E_T$ would be $+ 1{\cdot}58$ volt).

It may be noted that even when positive $E^\circ_T$ values are obtained, nothing can be predicted about the speed of a reaction. It may be that a predicted reaction proceeds so slowly that, in effect, there is no reaction. Certain other factors may also influence the reaction; for instance, with some metals a protective coating of oxide may form on the surface and stop further reaction.

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*Suppose the electrode potentials were given as reduction potentials, that is, with the reverse signs. Then, we would subtract $-0{\cdot}76$ volt from $+0{\cdot}34$ volt, *i.e.*, the e.m.f. $=0{\cdot}34-(-0{\cdot}76)=1{\cdot}10$ volt.

## Questions

1. (*a*) Define 'electrode potential'.

(*b*) Describe in brief the various factors which affect the value of electrode potential.

2. (*a*) What is meant by the *standard electrode potential* on the hydrogen scale ?

(*b*) Why is it necessary to fix the concentration of ions and temperature in setting up standard electrode potentials.

3. Describe how a standard hydrogen electrode is constructed? Does it have a potential of 0·000 volts ? Why has been this value assigned to it, then ?

4. (*a*) What is conveyed by the cell notation given below ?

$$\mathrm{Zn} \mid \mathrm{Zn}^{2+},\ 1\mathrm{M} \overset{\overset{e^-}{\rightarrow}}{\|} \mathrm{H}^{+},\ 1\mathrm{M} \mid \mathrm{H}^{2}(\mathrm{Pt}),\ 1\ \mathrm{atm}$$

(*b*) Show by means of chemical equations the reactions that take place in the above cell.

5. Explain why the standard electrode potential of zinc is given a positive sign and that of copper a negative sign.

6. What are the basic requirements of a cell for a continuous flow of electrons to occur ?

7. (*a*) Is it possible to build up a voltaic cell by using identical conductors for both poles in the same solution ?

(*b*) What is a concentration cell ? Explain the principle of its operation with the aid of an example.

8. What is an electrochemical series ? List two important uses of the series,

## Key

4. (*a*) This notation conveys the following information :
   (*i*) One half cell is zinc electrode dipping in a 1M solution of $\mathrm{Zn}^{2+}$ ions.
   (*ii*) The other half cell is a standard hydrogen electrode.
   (*iii*) Electrons flow from the zinc electrode to the hydrogen electrode. That is, the potential of zinc electrode is higher than that of the hydrogen electrode. As such zinc is the anode and hydrogen electrode the cathode.

(*b*) Anode reaction : $\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2e^-$

Cathode reaction : $2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{H}_2$

6. The two basic requirements are : (1) the two electrodes must have different potentials, and (2) the circuit must be complete.

7. (*a*) No; because both the poles will have the same electrode potential.

(*b*) A concentration cell consists of two half cells with the same two poles but different concentrations of the common ion around the poles. The electrode potential of the metal will be somewhat greater in the dilute solution and therefore, electrons will flow from it to the electrode dipping in the more concentrated solution. The flow of electrons will continue so long as the inequality in the concentration of ions in the two half cells remains.

## Problems

1. What is the e.m.f. of the cells composed of—
   (*i*) standard copper (—0·34 volt) and silver (—0·80 volt) electrodes, and
   (*ii*) standard chlorine (—1·06 volt) and bromine (—1·36 volt electrodes) ?

[Ans. +0·46 volt; +0·30 volt]

2. The electrode potentials for the following half-reactions are :

$$\text{Mg} \rightleftharpoons \text{Mg}^{2+} + 2e^- \qquad E^0 = +2{\cdot}36 \text{ volts}$$
$$\text{Al} \rightleftharpoons \text{Al}^{3+} + 3e^- \qquad E_0 = +1{\cdot}66 \text{ volts}$$

Product if the reaction $3\text{Mg} + 2\text{Al}^+ \rightarrow 3\,\text{Mg}^{2+} + 2\text{Al}$ will occur or not, and why.

[**Ans.** Reaction will occur since $E^\circ_T$ is positive, $+0{\cdot}70$ volt]

3. Can you expect the ferric ion, $\text{Fe}^{3+}$, to oxidize the $\text{Br}^-$ ion ? The potential for the half reaction $2\,\text{Br}^- \rightleftharpoons \text{Br}_2^+ + 2e^-$ is $-1{\cdot}09$ volts and for the half reaction $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + e^-$ is $-0{\cdot}77$ volt.

[No; the value of $E^\circ_T$ for the reaction $2\text{Br}^- + \text{Fe}^{3+} \rightarrow \text{Br}_2 + 2\text{Fe}^{2+}$ is negative, $-0{\cdot}32$ volt.]

4. Calculate the voltage, $E^\circ_T$, obtained when each of the following standard half-cells is combined (assume appropriate electrolytes in each case) : (*a*) hydrogen and iron (2) hydrogen and copper. Use table 5-1 for the value of electrode potentials.

[**Ans.** (*a*) $+0{\cdot}44$ volt, (*b*) $-0{\cdot}34$ volt.]

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## 6

# Chemical Kinetics and Chemical Equilibrium

Chemical reactions take place at vastly different rates. An explosion of dynamite that tears away the side of a hill occurs within a fraction of a second, and reaction involving ions, *e.g.*, neutralization of acids and bases, occur as fast as the solutions containing the reacting ions are mixed*. On the other hand, the oxidation of red phosphorus occurs so slowly at room temperature that we may say that, for all practical purposes, there is no reaction at all. Rusting of iron, digestion of food, and hardening of cement are some examples of slow reactions in common experience. *The branch of chemistry that deals with the rates of chemical reactions is called* **chemical kinetics**.

The study of reaction rates has many practical applications. For example, before a certain chemical reaction is adopted by the industry it is important to find conditions that give the desired product at a reasonable speed in order to be economically feasible. It also gives an insight into the 'mechanism' of a reaction', *i.e.*, in what sequence of steps (one or more) does the reaction possibly takes place.

## 1. Reaction Rate

Reactions are often described as slow, moderate, fast, etc. Such expressions, however, give only a qualitative idea of reaction rates. For precision, the reaction rates are described quantitatively.

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*Examples of such reactions are :

$$H^+ + OH^- \rightarrow H_2O \qquad \text{(neutralization)}$$

$$\left.\begin{array}{l} Ag^+ + Cl^- \rightarrow AgCl\downarrow \\ Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4 \end{array}\right[ \begin{array}{l}\text{precipitation} \\ \text{reactions}\end{array} \Big]$$

Recent measurements of the rates of such reactions show that they occur during intervals measured in milli-seconds ($1 \times 10^{-3}$ sec.) and micro-seconds ($1 \times 10^{-9}$ sec.).

*The rate or velocity of a chemical reaction is expressed in terms of the change in concentration of one of the reactants or products per unit of the time.*

Consider the reaction between carbon monoxide gas, CO, and nitrogen dioxide, $NO_2$, at 200°C. The products of the reaction are carbon dioxide, $CO_2$, and nitric oxide, NO, formed according to the equation

$$CO + NO_2 \rightarrow CO_2 + NO$$

As the reaction proceeds, the reddish-brown colour of the gaseous mixture due to nitrogen dioxide progressively fades. Since the other gases are colourless, the reaction rate can be determined by measuring the change in colour during a certain time interval. This change will indicate the quantity of $NO_2$ that has reacted during the time interval. Then,

$$\text{Reaction rate} = \frac{\text{quantity } NO_2 \text{ consumed}}{\text{time interval}}$$

$$= \text{quantity } NO_2 \text{ consumed per unit time}$$

Since substances react in equivalent quantities, the rate of reaction can be specified by the change in concentration of any of the reactants or the products Thus, in the foregoing example, the rate of reaction can be equally well expressed in terms of the consumption (or decrease in concentration) of CO or in terms of the appearance (or increase in concentration) of either product, $CO_2$ or NO. Which is used depends upon convenience of measurement. If the progress of the reaction is followed by measuring the production of carbon dioxide, the reaction rate would be expressed as follows :

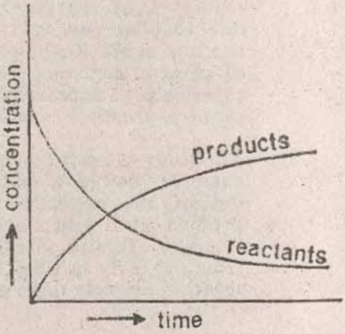


Fig. 6-1. Variation in concentrations of reactant and product with time in a chemical reaction.

$$\text{Reaction rate} = \frac{\text{quantity } CO_2 \text{ produced}}{\text{time interval}}$$

$$= \text{quantity } CO_2 \text{ produced per unit time.}$$

In measuring reaction rates concentrations are usually expressed as the number of moles of a substance in one litre. For example, if the concentration of a substance X in a reaction at a certain moment of time was 2·4 moles per litre and a minute later became 2·2 moles per litre, the rate of reaction equals 0·2 moles per minute. The time interval is expressed in whatever units fit the reaction : microseconds for the combustion of gasoline vapour mixed with air which is explosively rapid, seconds or minutes for the hydrolysis of an ester, and days for the rusting of iron.

## 2. Collision Theory of Reaction Rate

**2-1. Activation energy**. According to the collision theory of reaction rates, the reacting particles—ions or molecules must collide with each other before they can combine and effect a chemical change. Reactions between ions are extremely rapid. This is because the electrical field around ions extends equally in all directions and, therefore, each collision of oppositely charged ions results in chemical reaction. Since the number of collisions is very great (of the order $10^9$ times every second !), there is little delay in the reaction. The reactions involving covalently bonded molecules, by contrast, are very slow despite an equally high frequency of collisions. The reason is that not all collisions are effective. The only collisions that are effective are those in which the colliding molecules have sufficient energy to overcome the mutual repulsion of their electron clouds. *The minimum amount of energy that the molecules must possess for the collision to result in a chemical reaction is called the activation energy*, $E_a$. When the molecules with less energy collide, they fly apart unchanged. When the molecules having the necessary activation energy collide, their atoms are rearranged to form an intermediate, temporary product, called the activated complex Since some energy is absorbed in the formation of an activated complex, the complex necessarily contains more potential energy than the reactants. In an effective collision, the activated complex separates into products which have a new and more stable arrangement of atoms involved. This is shown diagrammatically in Fig. 6-2 where the collision between the molecules A-A and **B-B** results in the formation of two A-B molecules.

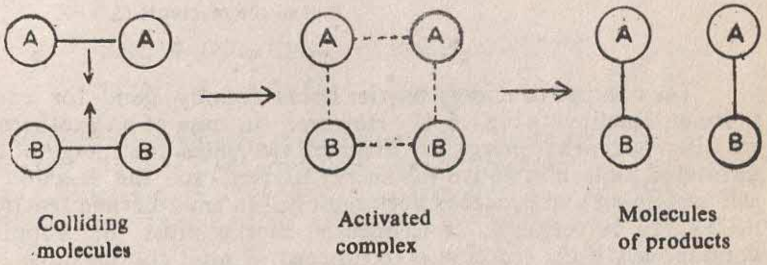


Fig. 6-2. Collision between high energy molecules A-A and B-B in proper orientation results in the formation of the activation complex which breaks up to yield the new A-B molecules. The dotted lines in the activated complex represent some sort of loose bonding in the molecular cluster of A-A and B-B.

**2-2. Energy barrier.** In an exothermic reaction, *e.g.*, the combination of hydrogen and oxygen, the combination of sulphur dioxide and oxygen, etc., the energy of the products is less than the energy of the reactants. Therefore, energy is evolved when an exothermic reaction occurs. Even so, an exothermic reaction will not occur spontaneously. There is an *energy barrier* that must be overcome before reaction can take place (Fig. 6-3). Thus, activation energy may be regarded as the energy needed to over come the energy barrier. This explains why a mixture of hydrogen and oxygen can stand in a container for years without a detectable reaction. If the mixture is ignited with a lighted taper, an explosion occurs as the reaction proceeds very rapidly. The lighted taper provides the energy to overcome the energy barrier.

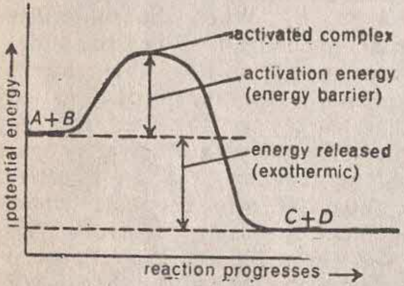


**Fig. 6-3.** Potential energy diagram for the exothermic reaction $A+B \rightarrow C+D+$ energy. Note that on this graph the total potential energy of the $(C+D)$ is lower than that of the reactants $(A+B)$.

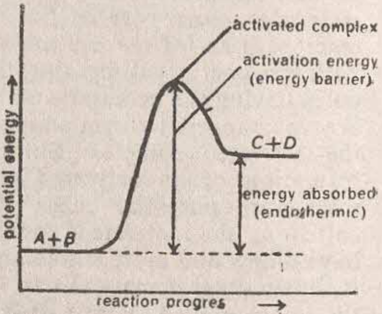
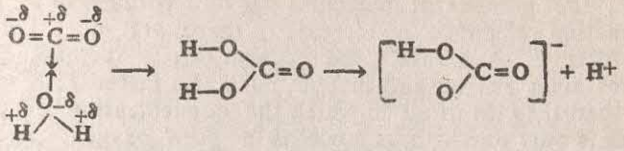


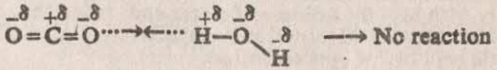
Fig. 6-4. Potential energy diagram for the endothermic reaction $A+B \rightarrow C+D -$ energy. Note that on this graph the total potential energy of the products $(C+D)$ is higher than that of the reactants $(A+B)$.

The concept of energy barrier holds equally good for endothermic reactions (Fig. 6-4). However, in case of an exothermic reaction sufficient energy is liberated to raise the energy of the unreacted molecules above the energy barrier; so, the reaction is self-sustaining and proceeds very rapidly. In endothermic reaction, no energy is released; consequently energy must be supplied continuously if the reaction is to proceed without cooling down.

**2-3. Orientation of collision.** The reacting molecules must not only collide with sufficient energy but must have the proper orientation if the reaction is to occur. This is just like the damage suffered by two colliding cars depends not only on their speeds (energy) but also on their directions or orientation. If the molecules collide in poor orientation, they simply bounce away from each other unchanged. Consider for example, the reaction between carbon dioxide and water. The water molecule is strongly dipolar. The carbon dioxide molecule as a whole is nonpolar, but its two carbon-oxygen bonds are polar. The effective collisions between these two molecules are those in which water's oxygen atom (negative) bumps into the carbon atom (positive) in carbon dioxide. Such collisions result in the formation of $H_2CO_3$ molecules which may further dissociate into $HCO_3^-$ and $H^+$ ions.



No reaction occurs as a result of collisions between molecules oriented such that one of water's positive hydrogen atom approaches one of carbon dioxide's oxygen atom.*



The proper orientation for effective collisions depends on the shapes of the molecules, the bond angles in them, and the polarity of the bonds that have to be broken.

## 3. Factors that Control Reaction Rates

Among all factors that control reaction rates, the one of fundamental importance is the nature of reactants. This is a factor that cannot be controlled, however, and thus is generally not considered as one of the factors that control reaction rates. The nature of reactants determines the amount of activation energy required for the reaction to occur and, therefore, the rate of reaction. For example, both nitric oxide and carbon monoxide combine with oxygen to form respective higher oxides. The reaction occurs at a moderate rate in the case of nitric oxide but so slowly in the case of carbon monoxide that no reaction appears to occur at all.

$$2NO + O_2 \rightarrow 2NO_2 \qquad \textit{moderate at } 20^\circ C$$

$$2CO + O_2 \rightarrow 2CO_2 \qquad \textit{extremely slow at } 20^\circ C$$

In general, reactions in which covalent bonds are broken tend to be slow due to a high activation energy; reactions of ions are usually very fast as they have an attraction for each other and, therefore, do not need additional energy to cause them to react.

The most frequently encountered rate-controlling factors are (*i*) concentration of reactants, (*ii*) particle size, (*iii*) temperature, and (*iv*) the presence of a catalyst. These factors may be considered in relation to the collision theory and the potential energy curve.

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*Theoretically, it is conceivable that this type of collision will result in the formation of an $OCOH^+$ ion and $OH^-$ ion. However, we find that $CO_2$ and $H_2O$ form a solution containing $H^+$ ion. Obviously, then, this collision does not result in a chemical reaction.

**3-1. Effect of concentration on reaction rate.** The frequency of collision between reacting molecules primarily depends upon the number of molecules present in a given volume. As the concentration, *i.e.*, the number of molecules per unit volume, of all or any of the reacting substance is increased, there are more collisions per unit of time. As a result, the reaction rate is increased. Thus, substances such as iron and carbon, burn at a faster rate in pure oxygen than they do in air in which the concentration of oxygen molecules is only one-fifth as much as in pure oxygen. A chip of marble will dissolve faster in 2M hydrochloric acid than in 1M hydrochloric acid.

**Experiment 1.** Preparcs a 0·3M solution of sodium thiosulphate. Dilute it separately with half the volume of water and twice the volume of water to obtain 0·2 M and 0·1 M solutions respectively. Also prepare a solution of hydrochloric acid of 2M concentration.

Using a burette, measure out 45 ml of 0·3 M sodium thiosulphate solution into a clean beaker. Add to this solution 5 ml of 2M hydrochloric acid with the help of a pipette, simultaneously starting the stop watch. Swirl the beaker once or twice to ensure thorough mixing of solutions, and place it over a piece of paper with a heavy black dot marked on it. Looking down vertically on to the beaker, note the time at which the black dot on the paper just disappears.

Repeat the experiment using the 0·2 M and 0·1 M solutions of sodium thiosulphate. You will find that the time decreases as the concentration is increased. (You can design a similar experiment using different concentrations of hydrochloric acid).

In the reaction between a solution of sodium thiosulphate and hydrochloric acid, the insoluble sulphur is precipitated in the from of slime.

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2 + S\downarrow$$

The precipitated sulphur causes the reaction mixture to become opaque. When this happens up to a certain level, the black dot cannot be seen through the mixture.

The results of this experiment show that the reaction rate (*i.e.*, the rate of formation of sulphur) increases as the concentration of thiosulphate is increased.

In considering the effect of concentration upon reaction rates, the concentrations are expressed in moles per litre. This is because a mole of any molecular substance consists of the same number of molecules and, therefore, the concentration of a substance expressed in moles per litre is a direct measure of the number of molecules per unit space.

The rate of any reaction progressively diminishes in time, since the reacting substances are gradually used up and their concentrations become lower and lower. Therefore, the velocity of a reaction refers to the velocity at a given moment.

**3-2. Effect of particle size on reaction rate.** A reaction between a solid and another substance can occur only on the surface of the particles of the solid where the reacting molecules collide, whether the other substance be solid, liquid, or gas. Consequently, the greater the surface area of the solid, the faster the reaction rate. Therefore, subdivision of the same quantity of a solid into smaller particles with larger total surface area results in faster reaction.* Thus, finely divided zinc reacts faster with acids than does coarse zinc, and finely powdered lead inflames spontaneously in air while a lump of lead metal remains unaffected. Similarly, large lumps of coal burn slowly, smaller pieces more rapidly, and powdered coal may burn at an explosive rate when ignited. The limit of subdivision is reached when the reacting substances are in the gaseous state or in solution as molecules or ions. This explains why reactions often occur more rapidly in gases or in solution.

In the reaction of a solid and a liquid, the reaction rate is often accelerated through shaking, mixing, or stirring whereby fresh portions of the reacting substances are brought into the reaction region.

**Experiment 2.** Weigh a piece of marble (about 2 g). Separately weigh identical quantities of coarsely powdered marble and finely powdered marble.

Place the piece of marble in a conical flask. Cover it with 50 ml of 2N-hydrochloric acid, simultaneously starting the stop watch. Swirl the liquid once every minute. Note the time it takes the marble piece to completely dissolve in the acid.

Repeat the experiment separately with the coarsely powdered marble and the finely powdered marble.

The reaction proceeds much faster when the marble particles are smaller in size.

**3-3. Effect of temperature on reaction rate.** Any rise in temperature increases the reaction rate. The reaction between hydrogen and oxygen takes place so slowly at ordinary temperatures that it does not seem to take place at all, but when a mixture of the gases is heated to 500°C, the reaction to from steam proceeds at a measurable rate. If the mixture is ignited, the reaction takes place explosively.

There are two reasons why a reaction would go faster at higher temperatures. First, temperature is a measure of the average kinetic energy of the particles in the reaction mixture. A rise in temperature increases the velocity of the particles and thereby the frequency of collisions between them. The increased frequency of collisions causes the rate of reaction to increase. Second and far more important reason, however, is that at the higher temperature a greater number of particles acquire the activation energy necessary for effective collisions. This point can be made clear by

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*The greater is the extent of subdivision, the greater is the increase in the total surface area of the resulting particles. Imagine a cube of marble of volume 1 $cm^3$. Each of its square face has an area of 1 $cm^2$; so, the total surface area of the cube is 6 $cm^2$. If this cube is broken into 1000 cubes, each of volume 1 $mm^3$, the total surface area exposed for the collision of reactant molecules would be $1000 \times 6\ mm^2 = 6000\ mm^2 = 60\ cm^2$, *i.e.*, sixty times the original area.

considering. Fig. 6-5 which shows the distribution of kinetic energies among the molecules of a gas at two different temperatures, $T$°C and $(T+10)$°C. If $E$ represents the activation energy of a particular reaction, there are nearly twice as many molecules (*a* versus *b*) having this energy at temperature (T+10)°C than at T°C.* As a general approximation, the reaction rate roughly doubles for each 10°C rise in temperature.

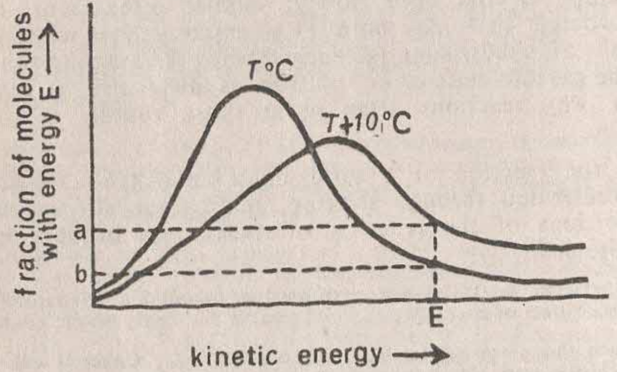

Fig. 6-5. Distribution of energy among the molecules of a gas at two different temperatures.

**Experiment 3.** Measure out 4 ml of 0·25 M sodium thiosulphate solution from a burette into each of three clean test tubes numbered 1,2, and 3, and measure out 4 ml of 0·25 M hydrochloric acid into each of three other test tubes numbered 1*a*, 2*a*, and 3*a*. Place all the test tubes in a beaker nearly half filled with water. Five minutes later, after measuring the temperature of the water (let it be $T$°C), pour the solution in test tube 1 into test tube 1*a*, simultaneously starting the stop watch. Shake the mixed solution once or twice and note the time it takes to turn opaque.

Heat the beaker with the test tubes to $(T+10)$°C and repeat the experiment, this time with test tubes 2 and 2*a*. Then carry out similar experiment with the test tubes 3 and 3*a* after raising the temperature by another 10°.

Note that the time decreases as the temperature is increased, that is, the reaction rate is increased at higher temperatures. By taking more sets of the two solutions you can show the effect of temperature on reaction rate by means of a graph, plotting the temperature as abcissa against time.

**3-4. Effect of catalyst on reaction rate**. A catalyst is a substance which, when added to the reacting substances, alters the reaction rate without being consumed. The phenomenon of the reaction rate being changed by a catalyst is called catalysis. Generally, a catalyst is used to speed a reaction, *e.g.*, platinum is

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*This argument is meaningful only for a slow reaction in which $E$ is well out on the tail of the curve, *i.e.*, only a small fraction of molecules possess the energy of activation. Suppose $E$ is near the peak of the curve or is even to the left it. This means that a large fraction of molecules already have the requisite energy so that most of the collisions are effective even at a lower temperature. The reaction, therefore, proceeds extremely rapidly and is said to be instantaneous.

used as catalyst to increase the rate of combination of sulphur dioxide and oxygen to sulphur trioxide : $SO_2\,(g)+O_2\,(g)\xrightarrow{Pt}SO(g)$. This is an example of *positive catalysis* and the catalyst is called a positive catalyst. In certain cases, a catalyst slows down a reaction. For example, if a little alcohol is added to sodium sulphite solution, its air oxidation to sodium sulphate is greatly retarded. A catalyst of this type is called negative catalyst and its action is termed *negative catalysis*.

According to the number of phases in the system, two kinds of catalysis are usually distinguished : homogeneous catalysis and heterogeneous catalysis.

In **homogeneous catalysis** the reactants and catalyst constitute a one phase system, such as a gaseous mixture or a liquid solution. Two examples of homogeneous catalysis are :

1. Combination of sulphur dioxide and oxygen in the presence of nitric oxide (gas-phase homogeneous catalysis).

$$2SO_2 + O_2 + (NO) \rightarrow 2SO_3 + (NO)^*$$

2. Hydrolysis of an ester in the presence of hydrogen ions, *i.e.*, an acid (*solution-phase homogeneous catalysis*).

$$\underset{\text{ester}}{R.COOR'} + H_2O + (H^+) \longrightarrow \underset{\text{acid}}{R.COOH} + \underset{\text{alcohol}}{R'OH} + (H^+)$$

In homogeneous catalysis the catalyst reacts with one of the reactants to form an intermediate substance which then reacts with the other reactant to give the product and regenerate the catalyst. Thus, in the presence of catalyst $K$ the reaction $A+B\rightarrow AB$ proceeds in two steps :

$$\begin{array}{ll} A + K \rightarrow AK & \text{(unstable intermediate compound)} \\ AK + B \rightarrow AB + K & \text{(regeneration of catalyst)} \\ \hline A + B + (K) \rightarrow AB + (K) & \end{array}$$

Each one of the two reactions in this scheme has a lower energy of activation than the uncatalyzed reaction and is, therefore, much faster.

The action of nitric oxide in increasing the rate of formation of sulphuric acid from sulphur dioxide, oxygen, and water may be described by the following equations for intermediate reactions :

$$\begin{array}{rl} O_2 + 2NO \rightarrow 2NO_2 & \text{(intermediate compound)} \\ 2SO_2 + 2H_2O + 2NO_2 \rightarrow 2H_2SO_4.NO & \text{(intermediate compound)} \\ 2H_2SO_4.NO \rightarrow 2H_2SO_4 + 2NO & \\ \hline 2SO_2 + O_2 + 2H_2O + (2NO) \rightarrow 2H_2SO_4 + (2NO) & \end{array}$$

Catalysts which act in the manner of nitric oxide in this reaction are called '*carrier catalysts*' (note that nitric oxide '**carries**' oxygen to sulphur dioxide for its oxidation).

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*The inclusion of (NO) on both sides of the equation shows that the catalyst is not used up in the reaction.

*In homogeneous catalysis the rate of reaction is practically proportional to the amount of the catalyst.*

In **heterogeneous catalysis** the reactants and the catalyst from a two-phase system. Some examples are :

1. Combination of nitrogen and hydrogen (both gases) in the presence of finely divided iron catalyst (solid phase).

$$N_2 + 3H_2 + (Fe) \rightarrow 2NH_3 + (Fe)$$

2. Hydrogenation of oils (liquid) in the presence of finely divided nickel (solid).

*Vegetable oils* + $H_2$ + (Ni) → *Vegetable ghee* + (Ni)

3. Combination of sulphur dioxide and oxygen (both gases) in the presence of finely divided platinum or vanadium pentoxide (solid)

$$2SO_2 + O_2 + (Pt) \rightarrow 2SO_3 + (Pt)$$

The catalysts used in heterogeneous catalysis are usually surface active solids, and are called 'contact catalysts'. Contact catalysts act by furnishing a surface at which the reacting molecules are absorbed. Adsorption of molecules on the catalyst surface reduces the energy necessary for activation so that more collisions are effective. Further, the increased concentration resulting from adsorption leads to more collisions per unit time, thus increasing the velocity of the reaction. The reaction products keep escaping from the catalyst surface making place for other reacting molecules. Thus, *in heterogeneous catalysis* relatively large amounts of reactants may react in the presence of small amounts of the catalyst and *the extent of catalytic action depends on the area of the* catalyst surface.

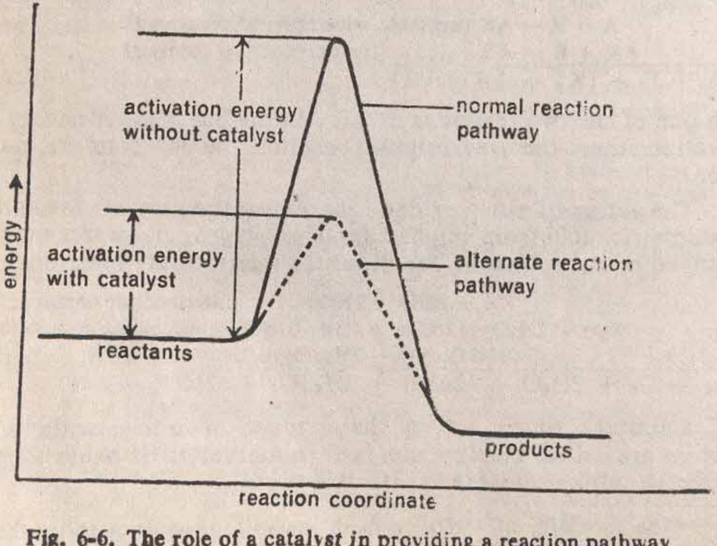

**Fig. 6-6. The role of a catalyst in providing a reaction pathway of lower activation energy.**

From the foregoing discussion, it is clear that the action of a catalyst can be explained in terms of the activotion energy. The catalyst offers the reacting molecules an alternative pathway of lower activation energy (Fig 6-6).* The lower the activation energy, the larger the proportion of reacting particles having the necessary energy and hence the faster the reaction.

A negative catalyst decreases the reaction rate by increasing the activation energy. It may also function by either removing the active intermediate products or by destroying some substance present in the reacting substance and acting as a positive catalyst.

**Experiment 4.** Pour 10 ml of 20 volume hydrogen peroxide in to each of four test tubes in a rack. Compare the effect of adding the following substances to the hydrogen peroxide in different test tubes by noting the rate at which bubbles of oxygen produced by the decomposition of hydrogen peroxide are evolved ($2H_2O_2 \rightarrow 2H_2O + O_2\uparrow$):

1. 2M NaOH (5 drops)
2. 2M HCl (5 drops)
3. manganese dioxide (about 0·1 gram)
4. aluminium powder (about 0·1 gram)

Note that all substances, except 2M HCl, speed up the decomposition of hydrogen peroxide. Confirm that the evolved gas is oxygen by testing with a glowing splint.

## 4. The Law of Mass Action

The quantitative relationship between reaction rate and concentration is expressed by the generalization referred to as the law of mass action. It was established experimentally by two Norwegian scientists, Guldberg and Waage, in 1867. The simplest form of the law is as follows :

*All other factors being equal, the rate of a chemical reaction is directly proportional to the product of the concentrations of the reacting substances.*

The concentrations are expressed in *moles per litre*. For gaseous substances the concentration can also be expressed in terms of their partial pressures in the reaction mixture. This is because the concentration of all gaseous components can be raised simultaneously by raising the pressure when the volume is decreased or lowered by lowering the pressure when the volume is increased by expansion.

For a reaction of the type $A \rightarrow B + C$ such as $PCl_5 \rightarrow PCl_3 + Cl_2$, the rate of reaction, R, will be directly proportional to the concentration of A, denoted as [A].** That is

$$R \propto [A] \quad \text{or,} \quad R = k \times [A]$$

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*In fact, the alternative pathway provided by the catalyst may involve several stages each of which has a lower energy of activation than the uncatalyzed reaction and is, therefore, relatively faster.

**In such symbols, the brackets mean 'molar concentration of', for example, $[PCl_5]$ means 'molar concentration of $PCl_5$'.

where $k$ is a proportionality factor, called the **rate constant**. The value of $k$ is equal to the rate of reaction when the molar concentration of the reactant A is 1. When the concentration of A is doubled, the rate of reaction is also doubled as there are now twice as many molecules undergoing decomposition per unit volume per unit time.

For a reaction of the type $A+B \rightarrow C$, such as $H_2+I_2 \rightarrow 2HI$, the expression for the reaction rate is,

$$R = k \times [A] \times [B]$$

When $[A]=1$ and $[B]=1$,

$$R = k$$

Thus the rate constant $k$. numerically equals the reaction rate when the molar concentrations of the reactants (or their products) equal unity.

**4-1. The case of coefficients.** If the equation for a reaction involves coefficients greater than 1 for the reacting molecules, the coefficients become exponents in the expression for the reaction rate. Thus, if a reaction proceeds as follows

$$2A + B \rightarrow A_2B$$

the reaction rate, according to the law of mass action, will be proportional to the product of $A \times A \times B$ as though the equation were written as

$$A + A + B \rightarrow A_2B$$

In such a case the concentration of A must appear twice in the rate equation :

$$R = k \times [A] \times [A] \times [B]$$
$$= k \times [A]^2 \times [B]$$

In the general case, when $m$ molecules of A react with $n$ molecules of B, *i.e.*, for the reaction represented by the equation

$$mA + nB \rightarrow C$$

the rate of reaction is expressed by the equation :

$$R = k \times [A]^m \times [B]^n$$

The value of $k$, the rate constant, is different for different reactions. For any given reaction, the value of $k$ remains the same so long as the temperature of the system does not change, and characterizes the influence of the nature of the reactants on the rate of the reaction between them. If the temperature is raised, the reaction rate becomes greater and the value of $k$ increases substantially.

**4-2. The case of solid reactants.** The conclusions concerning the influence of the concentrations of the reactants upon reaction rate do not apply to the reactants in the solid state. Since solid substances react only at their surface, the rate of reaction in the case of a solid substance depends on its surface area and not upon its bulk concentration. Therefore, if in a reaction solid substances are taking part along with gases and dissolved solids, the reaction rate depends only on the concentrations of the gaseous or dissolved substances, provided the state of subdivision of the solid remains the same. Thus, the rate of reaction of the combustion of coal

$$C+O_2 \rightarrow CO_2$$

is proportional only to the concentration of oxygen. That is, for this reaction

$$R=k[O_2]$$

**4-3. Explanation of the law of mass action on the basis of the collision theory.** Why is it that the reaction rate is governed by the *product* of the concentrations of the reacting substances and not by the *sum* of their concentrations ? The answer to this puzzling question is provided by the collision theory of reaction rate. According to this theory the reaction rate is determined by the number of effective collisions between the molecules of reactants, say A and B, per unit time. Now, suppose that each square in Fig. 6·7 represents a container of one unit volume, and that each white circle represents 1 molecule of the reactant A, and each black circle 1 molecule of reactant B. For the reaction to occur, it will be necessary for one molecule of A to collide with one molecule of B. If all other factors affecting reaction rate such as temperature, speed of molecules, etc. are equal, the chances for collision will be given by the numerical product of the number of A molecules and the number of B molecules in each container. This may be shown by drawing lines for all possible A and B collisions.

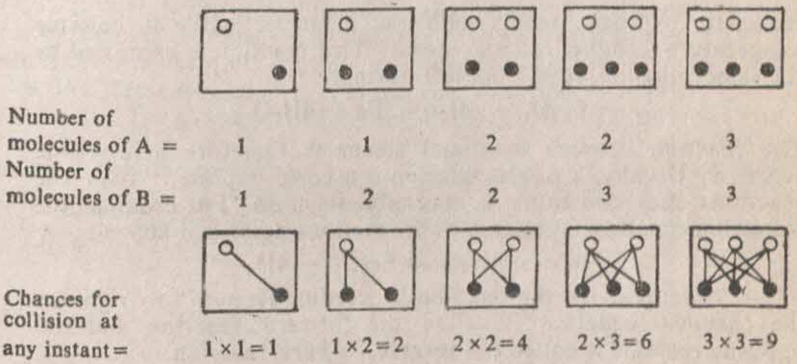
Number of molecules of A = 1 1 2 2 3
Number of molecules of B = 1 2 2 3 3
Chances for collision at any instant = 1×1=1 1×2=2 2×2=4 2×3=6 3×3=9

Fig. 6-7. The chances for collisions are equal to the numerical product of the number of A molecules and the number of B molecules in a given volume.

Since the number of effective collisions is a constant fraction of the total number of collisions, the reaction rate is directly proportional to the molar concentrations of the reacting substances.

## 5. Irreversible and Reversible Reactions

**5-1. Irreversible reactions.** In many chemical reactions the initial substances are transformed entirely into the reaction products. Such reactions are said *to go to completion*. For example, when potassium chlorate is heated it changes entirely into potassium chloride and oxygen

$$2KClO_3 \xrightarrow{\triangle} 2KCl + 3O_2 \uparrow$$

The reverse reaction, *i.e.*, the combination of potassium chloride and oxgyen to form potassium chlorate does not occur under any conditions known to us. *A chemical reaction which proceeds to completion, and in which the resulting products do not react to form the original substances is called an* **irreversible reaction.** Reactions in which a gas is given off, or an isoluble solid is formed, or in which water is one of the products, are irreversible reactions and go to completion. A few examples of such reactions are :

$$NaCl + H_2SO_4 \xrightarrow{\triangle} NaHSO_4 + HCl \uparrow$$
$$AgNO_3 + NaCl \rightarrow NaNO_3 + AgCl \downarrow$$
$$Fe + CuSO_4 \rightarrow FeSO_4 + Cu \downarrow$$
$$NaOH + HCl \rightarrow NaCl + H_2O$$

**5-2. Reversible reactions.** *Such reactions in which the products, once formed, react under the same conditions to form the original substances are called* **reversible reactions**. For example, when water vapour (steam) is passed over heated iron, magnetic oxide of iron ($Fe_3O_4$) and hydrogen result.

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

However, hydrogen reacts with the magnetic oxide at the same temperature forming iron and steam. This reaction is expressed by the same equation, read from left to right :

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$$

The reaction between iron and steam is therefore a reversible reaction. Usually, a single equation is used to represent both the reactions that constitute a reversible reaction. For example, the following equation represents both reactions described above :

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

Conventionally, the reaction proceeding from left to right in the chemical equation is called the **forward reaction** and the opposite reaction is called the **reverse**, or **back reaction**.

Some more examples of reversible reactions are

(*i*) $N_2O_4 \rightleftharpoons 2NO_2$

(*ii*) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(*iii*) $2SO_2 + O_2 \rightleftharpoons 2SO_3$

(*iv*) $CaCO_3 \rightleftharpoons CaO + CO_2$ (in a closed vessel)

(*v*) $\underset{\text{acetic acid}}{CH_3.COOH} + \underset{\text{ethyl alcohol}}{C_2H_5OH} \rightleftharpoons \underset{\text{ethyl acetate}}{CH_3COO.C_2H_5} + \underset{\text{water}}{H_2O}$

Unlike an irreversible reaction, a reversible reaction cannot go to completion in a closed system. That is, even though the reactants are taken in equivalent quantities, they are never used up completely to form the reaction products. However, if any one of the products is removed from the sphere of reaction as fast as it forms, a reversible reaction can go to completion. In lime kilns, limestone completely decomposes to yield calcium oxide and carbon dioxide as the latter continually leaves the reacting system.

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow$$

The reversible reaction $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$ can go to completion in the forward direction if the hydrogen is swept out of the reaction tube by the steam. On the other hand, the reverse reaction can go to completion if steam is swept out by the current of hydrogen.

## 6. Chemical Equilibrium—a Dynamic Steady State

For any reversible reaction in a closed system, an equilibrium is eventually established in which the rate of forward reaction is equal to the rate of the reverse reaction. Suppose a reversible reaction represented by the equation

$$A + B \rightleftharpoons C + D$$

is allowed to take placed at a particular temperature by placing A and B in a closed vessel. The rate of the forward reaction $(A + B \rightarrow C + D)$ will be initially proportionally to the molar concentrations of A and B. As more of the two reactants (A and B) are transformed into the products (C and D), the rate of the forward reaction decreases due to the decreasing concentrations of the reactants. The molecules of the products C and D formed will react to give A and B $(C + D \rightarrow A + B)$ at a rate proportional to the molecular concentrations of C + D which will, at first, be very

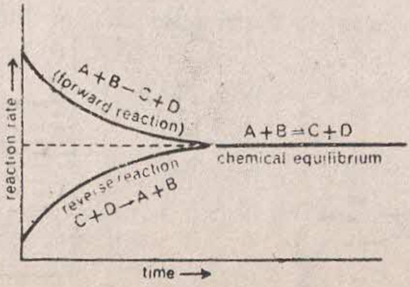

Fig. 6·8. Chemical equilibrium is reached when the rate of the forward reaction is equal to the rate of the reverse reaction.

low. As more of C and D will form in the forward reaction, however, the rate of the backward reaction will gradually increase. Eventually the two reactions reach a point where the rate at which A and B are reacting to form C and D is equal to the rate at which C and D are reacting to form A and B. This is the condition of *equilibrium* in which there is no change in reaction rate with time for either the forward reaction or the reverse reaction (Fig. 6-8). As a result, the concentrations of all the substances (A,B,C, and D) will remain unchanged. It must be kept in mind, however, that this is a *dynamic* state since the two reactions have not stopped but are continually taking place at an equal rate. There is no net change in the concentrations of various substances because each one is being formed as fast in one reaction as it is being used up in the opposite reaction.

**6-1. Features of chemical equilibrium.** The main features are :

1. Chemical equilibrium is reached when two opposite reactions proceed at exactly the same rate so that the concentrations of the substances in the reaction mixture remains unchanged. It is therefore a *dynamic steady state.**

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*The dynamic steady state can be compared with the equilibrium of water in a reservoir which is being simultaneously filled and discharged. If the rate of water flowing in equals the rate of water flowing out (Fig 6-9), the quantity of water in the reservior will remain unchanged like the quantities of substances in the reaction mixture when chemical equilibrium is attained. A reservoir in which water is neither entering nor flowing out does not represent a dynamic steady state although the quantity of water remains constant; it is simply a steady state but equilibrium does not exist (Fig. 6-10).

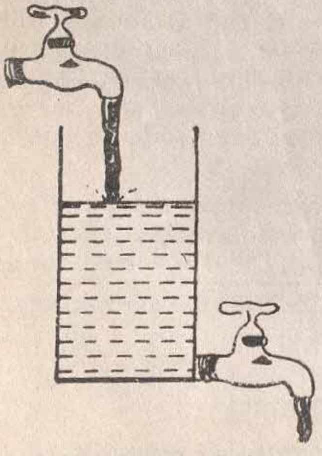


Fig. 6-9. Dynamic steady state.

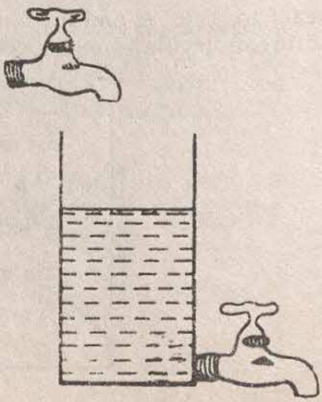


Fig. 6-10. Static steady state.

2. The same equilibrium can be attained from either side. Suppose, we start the reaction $A + B \rightleftharpoons C + D$ with 1 mole each of A and B, and when the equilibrium is attained at T°C the system contains 0·6 mole each of A and B, and 0·4 mole each of C and D. If we start with 1 mole each of C and D, the equilibrium at T°C will have the same composition : 0·6 mole each of A and B, and 0 4 mole each of C and D.

3. A chemical equilibrium, once established between any given substances, will last indefinitely if the conditions remain unchanged.

4. The equilibrium concentrations change with changes in conditions such as the temperature but spontaneously go back to the original level when the disturbing factors are removed.

5. Equilibrium can be attained only in a 'closed system'—*a system containing a constant amount of matter with all of this matter at the same temperature.*

## 7. Equilibrium Constants

Consider a reversible reaction expressed by the general equation :

$$mA + nB \rightleftharpoons xC + yD$$

where A and B are two substances which react to form two new substances C and D, and that C and D react under the same conditions forming the original substances A and B. Let us assume that the concentations of these four substances, respectively, are [A], [B], [C], and [D], and that the temperature remains constant throughout. Then, applying the law of mass action (the reaction rate is proportional to the product of the concentrations of the reacting substances).

rate of the forward reaction, $R_1 = k_1 \,.\, [A]^m \,.\, [B]^n$

rate of the backward reaction, $R_2 = k_2 \,.\, [C]^x \,.\, [D]^y$

where $k_1$, and $k_2$ are the rate constants of the forward and backward reactions respectively.

When equilibrium is established the rates of both reactions become equal, *i.e.*, $R_1 = R_2$.

That is, $$k_1 \,.\, [A]^m \,.\, [B]^n = k_2 \,.\, [C]^x \,.\, [D]^y$$

or, $$\frac{[C]^x \,.\, [D]^y}{[A]^m \,.\, [B]^n} = \frac{k_1}{k_2}$$

Because $k_1$ and $k_2$ are constant, the ratio $k_1/k_2$ is also constant, and the expression may be written

$$\frac{[C]^x \,.\, [D]^y}{[A]^m \,.\, [B]^n} = K_c$$

The constant $K_c$ is called the **equilibrium constant.** It may be defined as *the ratio of the product of the molar concentrations of the products to the product of the molar concentrations of the reactants in the state of chemical equilibrium.* It is a value specific for each reaction and does not depend on the concentration. However, since it is given by the ratio of two reaction rates $k_1$ and $k_2$, and these usually alter to a different degree when temperature is varied, $K_c$ varies with temperature. At a given temperature $K_c$ remains constant.

In deriving the equilibrium constant, it is required by convention to have the product of the concentrations of the products as the numerator. If, the product of the concentrations of reactants is taken as the numerator, we shall still obtain a constant. But, it would not be the equilibrium constant; it would be the reciprocal of it. Thus, for the reaction $A + B \rightleftharpoons C + D$, the expression

$$\frac{[A]\,[B]}{[C]\,[D]}$$

represents the reciprocal of the equilibrium constant, *i.e.*, $\frac{1}{K_c}$

**7-1. Equilibrium constants in terms of partial pressures**. For equilibrium reactions involving gases, the equilibrium contants can also be written in terms of the partial pressures of the gases rather than as molar concentrations. The equilibrium constant in terms of partial pressures is derived as $K_p$ For example, for the equilibrium reaction between nitrogen gas and hydrogen gas forming ammonia,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

the equilibrium constant can be written as either

$$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} \text{ or, } K_p = \frac{P_{NH_3}{}^2}{P_{N_2} \cdot P_{H_2}{}^3}$$

where $P$ represents partial pressure.

**7-2. Units of equilibrium constants**. Equilibrium constants may or mav not have units. For reactions in which the total number of moles of reactants is equal to the total number of moles of products, $K_c$ or $K_p$ bas no units. Thus, in the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$K_c$ would a pure number, *i.e.*, without units, since

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]} = \frac{(\text{mol}/l)^2}{(\text{mol}/l)\,(\text{mol}/l)}$$

Likewise, $K_p$ will also be dimensionless and a pure number.

In reactions in which there is a change in the number of moles, equilibrium constant will have units—$K_c$ will have units pertaining to concentration and $K_p$ will have units pertaining to pressure. Thus, for the equilibrium

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

Therefore, units of $K_c = \frac{(mol/l)^2}{(mol/l)\,(mol/l)^3}$ or $l^2\ mol^{-2}$.

The units of $K_p$ for this reaction will be atmospheres$^{-2}$ or $atm^{-2}$.

**7-3. Homogeneous and heterogeneous equilibria.** If all reactants and products form a homogeneous system consisting of a single phase, the equilibrium is said to be a *homogeneous equilibrium*. Such reactions take place in gas mixtures or liquid solutions. For example, the reaction of nitrogen gas and hydrogen gas in equilibrium with ammonia gas, or the hydrolysis of ester in which the ester, water containing $H^+$ ions, and the resulting acid and alcohol are all miscible liquids are examples of homogeneous equilibria.

On the other hand, if one or more of the reactants or products be in a different phase than the other species, the equilibrium is said to be a *heterogeneous equilibrium*. Examples of heterogeneous equilibria are furnished by the following examples :

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(g) + 4H_2(g)$$
$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

In heterogeneous equilibria, the solids are not included in the equilibrium constant expression. The reason is that in the heterogeneous system *gas-solid* the molecules of the gas can collide with the molecules of the solid only at the interface; hence, the concentration of the solid as a whole has no effect on the reaction rate. Thus, for the reaction between heated carbon and carbon dioxide

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

the equilibrium constant $K_c = \frac{[CO]^2}{[CO_2]}$

The equilibrium state of this reaction is not affected by an increase or decrease in the quantity of coal; it can be disturbed only by changing the concentration of carbon dioxide or carbon monoxide.

For the reactions

$$S(s) + O_2(g) \rightleftharpoons SO_2(g)$$

and, $$CaCO_3(s) \rightleftharpoons CaO(g) + CO_2(g)$$

the equilibrium constants are

$K_c = \frac{[SO_2]}{[O_2]}$ and $K_c = [CO_2]$ respectively

**7-4. Determination of equilibrium constants.** The value for a particular equilibrium constant can be determined by measuring the concentrations of all reactants and products at equilibrium, at a given temperature. As one example, examine the reversible reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

For a given mixture of $N_2$, $H_2$, and $NH_3$ at 300°C and 300 atm pressure, it was found by analysis at equilibrium that there are 0·3 mole $N_2$, 0·9 mole $H_2$, and 1·4 moles $NH_3$ per unit volume. Substituting these values in the equilibrium constant expression for this system,

$$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} = \frac{(1{\cdot}4)^2}{(0{\cdot}3)\,(0{\cdot}9)^3} = 9{\cdot}0 \text{ approximately}$$

Hence, the equilibrium constant for the system under specified conditions has the value 9·0. If we start with just $NH_3$ at any molar concentration, or with any mixture of $N_2$ and $H_2$, or with any mixture of $N_2$, $H_2$, and $NH_3$ and let the system remain at 300°C and 300 atm pressure until equilibrium is attained, the molar concentrations of the three substances will be such that the quotient $[NH_3]^2/[N_2]\,[H_2]^3$ will be equal to 9·0.

**7-5. Significance of equilibrium constant.** The value of equilibrium constant has a twofold significance :

1. *The value of $K_c$ is a measure of the extent to which the reversible reaction has proceeded at equilibrium.* The larger the value of the equilibrium constant, the greater is the extent to which the forward reaction takes place and, therefore, the greater the concentration of the products at equilibrium. A small equilibrium constant would likewise indicate that the forward reaction takes place only to a small extent and therefore only a small amount of the products is being formed at equilibrium.

2. *Knowing the value of the equilibrium constant and the initial concentrations of the reacting substances, the concentrations of various substances at equilibrium can be easily calculated.* This is illustrated in the example 4 given on page 176.

## 8. Shift of Equilibrium

The equilibrium constant for a given reaction at equilibrium must remain constant at a given temperature. Therefore, if any change in conditions causes a change in the concentration of any of the products or reactants, the concentrations of other substances must also change in such a way as to compensate for this. *The change of concentration caused by a disturbance of equilibrium is called a shift or displacement of equilibrium.* If the concentrations of the substances in the right half of the equation increase (obviously, with a corresponding decrease in the concentrations of the substances in the left), the equilibrium is said to have *shifted to* *the right* or in the direction of the forward reaction. On the other hand, if the concentrations undergo the opposite change, the equilibrium is said to have shifted to the left.

**8·1. Effect of change in concentration on equilibrium.** When the concentrations of the components of a system in equilibrium are changed, the value of $K_c$ does not change but the equilibrium is changed, because either the forward or the backward reaction rate is favoured. The equilibrium constant expressions can, therefore, be used to determine which way the equilibrium will shift if the concentration of any of the substances in the system is changed. Consider the equilibrium

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

for which $K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$.

Suppose that after equilibrium is attained, an additional quantity of $N_2$ is introduced. This causes an increase in the value of $[N_2]$ and thereby in the value of the denominator in the equilibrium constant expression. Since the value of $K_c$ at a given temperature remains constant, the concentration of $H_2$ must decrease and the concentration of $NH_3$ must increase. That is, the equilibrium is shifted to the right—the direction in which $N_2$ and $H_2$ combine to form $NH_3$. In the new equilibrium, the concentration of $H_2$ will be lower than it was before $N_2$ was added, while the concentration of $NH_3$ will be higher. The equilibrium will similarly shift to the right if the concentration of $H_2$ is increased or that of $NH_3$ is decreased. On the other hand, increasing the concentration of $NH_3$ or decreasing the concentration of $N_2$ and $H_2$ will cause the equilibrium to shift to the left, *i.e.*, towards the decomposition of ammonia and formation of new quantities of $N_2$ and $H_2$. In a general reversible reaction $A+B \rightleftharpoons C+D$ for which

$$K_c = \frac{[C]\,[D]}{[A]\,[B]}$$

the equilibrium will shift to the right if the concentrations of A and B are increased or the concentrations of C and D are decreased, and to the left if the concentrations of A and B are decreased or the concentrations of C and D are increased. Two very important conclusions can be drawn from these considerations :

(*a*) If one of the reactants of a reversible reaction is sought to be used up more completely, an excess of the other reactant must be used.

(*b*) If one of the products is continually removed from the sphere of reaction, the equilibrium will shift towards the formation of that product. On this basis, a reversible reaction can be made to go to completion. For example, if the water vapour formed in the reversible reaction between carbon dioxide and hydrogen

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

is continually removed from the reaction mixture, these gases can be entirely converted into carbon monoxide and water vapour.

**8·2. Effect of change of pressure on equilibrium**. Changes in pressure affect the equilibrium state measurably only when gases are involved, and in such cases only when the chemical reaction is accompanied with a change in the total number of molecules in the system. Examples of such systems are :

(*i*) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (total number of molecules on the left 4; on the right 2)

(*ii*) $N_2O_4 \rightleftharpoons 2NO_2$ (total number of molecules on the left 1; on the right 2)

With the increase in the pressure on a gaseous system the volume decreases and the concentrations of substances in moles per litre and the total number of molecules per unit volume increase. As such, the reaction that involves a decrease in the total number of molecules (per unit of volume) will be accelerated causing a new equilibrium to be established. In the above examples, an increase in pressure will favour formation of ammonia and suppress the dissociation of nitrogen tetroxide; a decrease in pressure will have opposite effects.

**8-3. Effect of change in temperature on equilibrium.** The equilibrium concentrations are affected if the temperature is altered. For an exothermic reaction, heat can be considered as one of the products; for an endothermic reaction as a reactant. In every system in equilibrium two reactions occur simultaneously one of which is exothermic and the other one endothermic. The exothermic reaction is favoured by a decrease in temperature, the endothermic reaction is favoured by an increase in temperature. Any change in the temperature of a system in equilibrium causes the two opposite reactions to proceed at unequal rates. The system remains out of equilibrium until the reaction rates again become equal when a new equilibrium state is established.

For example, in the equilibrium represented by the equation

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \triangle$$

if the temperature is raised, the equilibrium will shift to the left, the equilibrium constant will change, the concentration of ammonia will decrease, and the concentrations of hydrogen and nitrogen will increase. Conversely, lowering the temperature will cause the equilibrium to shift to the right and consequently the equilibrium constant will change, the concentration of ammonia will increase, and the concentrations of nitrogen and hydrogen will decrease.

**8-4. Effect of catalyst on equilibrium.** The addition of a catalyst to a system at equilibrium does not alter the equilibrium concentrations and the equilibrium constant remains unchanged. This is because any catalyst affects the rates of both the forward and the reverse reactions to the same extent.

In section 3-4, page 152, the effect of catalysts on reaction rates was discussed in terms of lowering the activation energy. In altering the pathway of the reaction, the catalyst lowers the activation energy of the forward reaction, and at the same time lowers the activation energy for the reverse reaction by an equal amount (Fig. 6-11). The catalyst is thus effective in increasing the reaction rate in both directions, forward and reverse, and thereby hastening the approach of equilibrium.

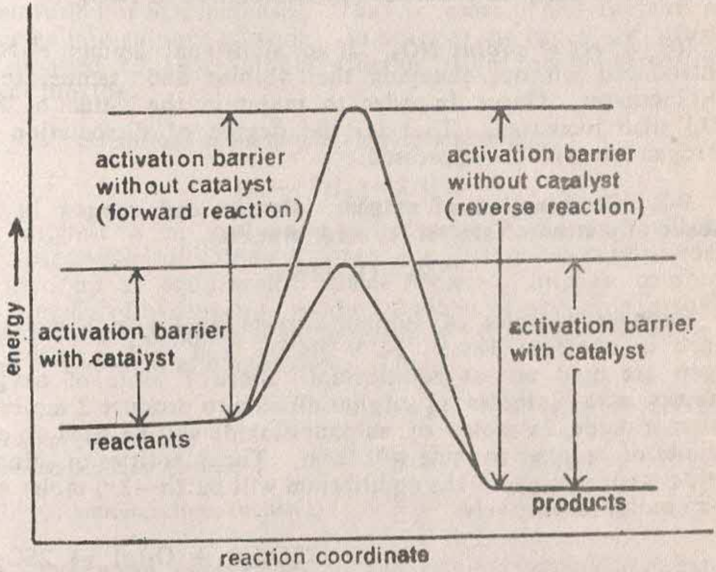


Fig. 6-11. The role of a catalyst in a reversible reaction.

## 9. Equilibrium Constants for Certain Equilibria

**9-1. The Dissociation of dinitrogen tetroxide, $N_2O_4 \rightleftharpoons 2NO_2$.** Let '*a*' moles of $N_2O_4$ be heated in a closed vessel of volume V liters, and let '*x*' moles of it be dissociated at equilibrium. Since 1 mole of $N_2O_4$ dissociates to produce 2 moles of $NO_2$, *x* moles of $N_2O_4$ will dissociate to produce 2*x* moles of $NO_2$

| | $N_2O_4(g) \rightleftharpoons$ | $2NO_2(g)$ |
|---|---|---|
| **Initial amounts (moles) ;** | $a$ | $o$ |
| **Equilibrium amounts (moles) :** | $(a-x)$ | $2x$ |
| **Equilibrium concentrations (moles/l) :** | $\frac{(a-x)}{V}$ | $\frac{2x}{V}$ |

Substituting these values in the equilibrium constant expression,

$$K_c=\frac{[NO_2]^2}{[N_2O_4]}=\frac{\left(\frac{2x}{V}\right)^2}{\frac{(a-x)}{V}}=\frac{4x^2}{(a-x)V}$$

(*i*) *Effect of change in pressure.* The expression for $K_c$ for the dissociation of dinitrogen tetroxide has V in the denominator. When pressure is increased, the volume V decreases, and since $K_c$ at a given temperature remains constant, $x$ also decreases. That is, increase in pressure suppresses the dissociation of $N_2O_4$. Conversely, decrease in pressure enhances the dissociation of $N_2O_4$.

(*ii*) *Effect of adding $NO_2$.* If an additional amount of $NO_2$ is introduced without changing the volume and temperature, $[NO_2]$ increases. Hence, in order to maintain the value of $K_c$, $[N_2O_4]$ also increases. That is, the degree of dissociation of dinitrogen tetroxide is suppressed.

**9-2. Combination of sulphur dioxide and oxygen in the presence of platinum catalyst (contact process),**

$$2SO_2+O_2\rightleftharpoons 2SO_3.$$

Suppose '*a*' moles of sulphur dioxide react with '*b*' moles of oxygen in a closed vessel of V litres, and that $x$ moles of oxygen are used up at equilibrium. Since 1 mole of oxygen combines with 2 moles of sulphur dioxide to produce 2 moles of sulphur trioxide, $2x$ moles of sulphur dioxide will be used up and $2x$ moles of sulphur trioxide will form. The quantities of sulphur dioxide and oxygen at the equilibrium will be $(a-2x)$ moles and $(b-x)$ moles respectively.

| | $2SO_2(g)$ + | $O_2(g)$ $\rightleftharpoons$ | $2SO_3(g)$ |
|---|---|---|---|
| Initial amounts (moles) : | $a$ | $b$ | $o$ |
| Equilibrium amounts (moles) : | $(a-2x)$ | $(b-x)$ | $2x$ |
| Equilibrium concentrations (moles/1) : | $\frac{(a-2x)}{V}$ | $\frac{(b-x)}{V}$ | $\frac{2x}{V}$ |

Substituting these values in the equilibrium constant expression

$$K_c=\frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

$$=\frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-2x}{V}\right)^2\left(\frac{b-x}{V}\right)}=\frac{4x^2.V}{(a-2x)^2(b-x)}$$

(*i*) *Effect of change in pressure.* When pressure is increased, the volume 'V' decreases. Hence, in order to maintain the value of $K_c$, $x$ increases. That is, increase in pressure favours the combination of sulphur dioxide and oxygen to form sulphur trioxide. Any decrease in pressure will have the opposite effect.

(*ii*) *Effect of adding sulphur dioxide or oxygen.* Addition of sulphur dioxide or oxygen to the equilibrium mixture without changing the volume and the temperature will increase the denominator in the equilibrium constant expression

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

Hence, in order to maintain the value of $K_c$, the numerator, *i.e.*, the concentration of $SO_3$ increases. That is, more of the reactants are converted into sulphur trioxide. In practice, an excess of oxygen (air) is used so that sulphur trioxide is entirely converted into sulphur dioxide.

### 9-3. Synthesis of ammonia (Haber's process).

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Suppose '*a*' moles of nitrogen react with '*b*' moles of hydrogen in a closed vessel of volume V litres, and that $x$ moles of nitrogen are used up at equilibrium. Since. 1 mole of nitrogen combines with 3 moles of hydrogen to produce 2 moles of ammonia, $x$ moles of nitrogen will combine with $3x$ moles of hydrogen to produce $2x$ moles of ammonia at equilibrium, Then,

| | $N_2(g)$ + | $3H_2(g)$ ⇌ | $2NH_3(g)$ |
|---|---|---|---|
| Initial amounts (moles) : | $a$ | $b$ | $o$ |
| Equilibrium amounts (moles) : | $(a-x)$ | $(b-3x)$ | $2x$ |
| Equilibrium concentrations (moles/l) : | $\frac{(a-x)}{V}$ | $\frac{(b-3x)}{V}$ | $\frac{2x}{V}$ |

Substituting these values in the equilibrium constant expession,

$$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

$$= \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3} = \frac{4x^2 \,.\, V^2}{(a-x)\,(b-3x)^3}$$

(*i*) *Effect of change in pressure.* If pressure is increased, the volume V decreases. Hence, in order to maintain the value of $K_c$, $x$ must increase. That is, increase in pressure favours the conversion of nitrogen and hydrogen into ammonia.

*(ii) Effect of adding nitrogen or hydrogen.* Addition of nitrogen or hydrogen to the equilibrium mixture without changing the volume and the temperature will increase the denominator in the equilibrium constant expression

$$K_c=\frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

Hence, in order to maintain the value of $K_c$, the numerator, *i.e.*, the concentration of $NH_3$ increases. That is, more of the reactants are converted into ammonia. In practice, nitrogen is used in excess.

### 9-4. Hydrolysis of Ethyl Acetate

$$\underset{\text{ethyl acetate}}{CH_3.COOC_2H_5} + \underset{\text{water}}{H_2O} \rightleftharpoons \underset{\text{acetic acid}}{CH_3.COOH} + \underset{\text{ethyl alochol}}{C_2H_5OH}$$

Let $a$ moles of ethyl acetate react with $b$ moles of water in volume V litres, and let $x$ moles of acetic acid and $x$ moles of ethyl alcohol be present when the state of equilibrium is reached.

$$CH_3.COOC_2H_5+H_2O \rightleftharpoons CH_3.COOH+C_2H_5OH$$

| | | | | |
|---|---|---|---|---|
| Initial amounts (moles) : | $a$ | $b$ | $o$ | $o$ |
| Equilibrium amounts (moles) : | $(a-x)$ | $(b-x)$ | $x$ | $x$ |
| Equilibrium concentrations : (moles/l) | $\frac{(a-x)}{V}$ | $\frac{(b-x)}{V}$ | $\frac{x}{V}$ | $\frac{x}{V}$ |

Substituting these values in the equilibrium constant expression

$$K_c=\frac{[CH_3.COOH]\,[C_2H_5OH]}{[CH_3.COOC_2H_5]\,[H_2O]}$$

$$=\frac{\frac{x}{V}\times\frac{x}{V}}{\left(\frac{a-x}{V}\right)\cdot\left(\frac{b-x}{V}\right)}=\frac{x^2}{(a-x)\,(b-x)}$$

Since the volume term V cancels and does not appear in the expression for $K_e$, the equilibrium is not affected by a change in volume or pressure. It is also obvious that increasing the concentration of water will favour the hydrolysis of ethyl acetate as it will lead to an increase in the concentration of $CH_3.COOH$ and $C_2H_5OH$ to maintain the value of $K_c$ in the expression

$$K_c=\frac{[CH_3.COOH]\,[C_2H_5OH]}{[CH_3.COOC_2H_5]\,[H_2O]}$$

## 10. Le Chatelier's Principle

The qualitative influence of various factors on a system in equilibrium was generalized by Le Chatelier in 1888 in what is known as Le Chatelier's principle. This may be stated thus :

*When a system in equilibrium is subjected to a change in temperature, pressure, or concentration of a component, the equilibrium shifts in the direction of the reaction opposing that change.*

Thus, in a system in equilibrium—

(1) *Increase in pressure* shifts the equilibrium towards the reaction proceeding with decrease in volume so that the total volume of the system is reduced, *e.g.*, to the right in the system

$$\underbrace{\begin{array}{ccc} 2SO_2(g) & + & O_2(g) \\ 2\text{ mol.} & & 1\text{ mol.} \\ 2\text{ vol.} & & 1\text{ vol.} \end{array}}_{3\text{ vol.}} \rightleftharpoons \underset{2\text{ vol.}}{\begin{array}{c} 2SO_3(g) \\ 1\text{ mol.} \\ 2\text{ vol.} \end{array}}$$

and to the left in the system

$$\underset{1\text{ vol.}}{\begin{array}{c} PCl_5(g) \\ 1\text{ mol.} \\ 1\text{ vol.} \end{array}} \rightleftharpoons \underbrace{\begin{array}{ccc} PCl_3(g) & + & Cl_2(g) \\ 1\text{ mol.} & & 1\text{ mol.} \\ 1\text{ vol.} & & 1\text{ vol.} \end{array}}_{2\text{ vol.}}$$

*Decrease in pressure* shifts the equilibrium towards the reaction in which volume and, therefore, the pressure increases, *e.g.*, to the right in the system

$$\begin{array}{ccc} N_2O_4(g) & \rightleftharpoons & 2NO_2(g) \\ 1\text{ mol.} & & 2\text{ mol.} \\ 1\text{ vol.} & \rightleftharpoons & 2\text{ vol.} \end{array}$$

Change in pressure has no effect on equilibrium if the total volume of the products is the same as that of the reactants, *e.g.*, in the system

$$\underbrace{\begin{array}{ccc} CO(g) & + & H_2O(g) \\ 1\text{ mol.} & & 1\text{ mol.} \\ 1\text{ vol.} & & 1\text{ vol.} \end{array}}_{2\text{ vol.}} \rightleftharpoons \underbrace{\begin{array}{ccc} CO_2(g) & + & H_2(g) \\ 1\text{ mol.} & & 1\text{ mol.} \\ 1\text{ vol.} & & 1\text{ vol.} \end{array}}_{2\text{ vol.}}$$

(2) *Increase in temperature* shifts the equilibrium towards the reaction which will lower the temperature, *i.e.*, which proceeds with the absorption of heat (endothermic reaction), *e.g.*, to the right in the system

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) - 43{,}200\text{ cal.}$$

and to the left in the system

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 22{,}400\text{ cal.}$$

Decrease in temperature shifts the equilibrium towards the reaction in which heat is evolved (exothermic reaction), *e.g.*, to the right in the system

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 46{,}800\text{ cal.}$$

(3) *Increase in the concentration* of any component in the system shifts the equilibrium in the direction of the reaction in which it is used up, *i.e.*, in which its concentration decreases. For example, in the equilibrium $A + B \rightleftharpoons C + D$, any increase in the concentration of A or B at the equilibrium will shift it in the direction of the forward reaction; any increase in the concentration of C or D will shift it in the reverse direction.

(4) A *catalyst* accelerates the forward and the reverse reactions to equal extent. Hence, introduction of a catalyst into a system at equilibrium has no effect upon it. However, a catalyst helps the equilibrium to be reached in less time at a given temperature by increasing the rates of both the forward and the reverse reactions.

**10-1. Applications of Le Chatelier's principle.** Le Chatelier's principle is of great value in predicting the conditions for maximum yield of a particular product in a reversible reaction. This is illustrated in the following examples.

(1) **Synthesis of ammonia (Haber's process).** The formation of ammonia from nitrogen and hydrogen is an *exothermic* reaction which proceeds with a *decrease in volume*, and is *reversible*.

$$\begin{array}{ccccccc} N_2(g) & + & 3H_2(g) & \rightleftharpoons & 2NH_3(g) & + & 22{,}400 \text{ cal.} \\ 1 \text{ vol.} & & 3 \text{ vol.} & & 2 \text{ vol.} & & \end{array}$$

High pressure will favour the forward reaction, *i.e.*, the formation of ammonia, because it results in a decrease in volume. High temperature will favour the reverse endothermic reaction, *i.e.*, the dissociation of ammonia into its elements. Low temperature will favour the forward reaction which is accompained with evolution of heat. Increase in the concentration of nitrogen or hydrogen will favour the forward reaction in which they are used up and their concentrations decrease. In practice an excess of nitrogen is used with the hydrogen. To summarise, the favourable conditions for the highest possible yield of ammonia by the combination of nitrogen and hydrogen are : (1) *high pressure*, (2) *low temperature*, and (3) *excess of nitrogen* in the reacting gases.

(2) **Formation of sulphur trioxide from sulphur dioxide and oxygen (contact process).** This, too, is an exothermic, reversible reaction which proceeds with a decrease in volume.

$$\begin{array}{ccccccc} 2SO_2(g) & + & O_2(g) & \rightleftharpoons & 2SO_3(g) & + & 46{,}800 \text{ cal.} \\ 2 \text{ mol.} & & 1 \text{ mol.} & & 2 \text{ mol.} & & \end{array}$$

$$\underbrace{\begin{matrix} 2 \text{ vol.} & \qquad & 1 \text{ vol.} \end{matrix}}_{3 \text{ vol.}} \qquad \begin{matrix} 2 \text{ vol.} \\ \rightleftharpoons 2 \text{ vol.} \end{matrix}$$

Again, application of high pressure will shift the equilibrium to the right because the volume is reduced as the left-to-right reaction proceeds. Higher temperature will favour the right-to-left reaction; lower temperature will promote the combination of sulphur dioxide and oxygen—the exothermic reaction. If a large excess of oxygen is added to the system, the equilibrium will further shift to the right causing more of sulphur trioxide to be converted into sulphur trioxide. Thus, the optimum conditions for a high yield of sulphur trioxide from a given amount of sulphur dioxide are : (*i*) *high pressure*, (*ii*) *low temperature*, and (*iii*) *a large excess of oxygen* (or air).

(3) **Synthesis of nitric oxide** (*Birkland and Eyde process*). The combination of nitrogen and oxygen to form nitric oxide is a highly *endothermic*, reversible reaction which takes place with *no change in volume*

$$\begin{array}{lcll} N_2(g) \;+ & O_2(g) & \rightleftharpoons & 2NO(g) - x\text{ cal.} \\ 1\text{ mol.} & 1\text{ mol.} & & 2\text{ mol.} \\ \underbrace{1\text{ vol.} \qquad\quad}_{2\text{ vol.}} & \underbrace{1\text{ vol.}}_{} & \rightleftharpoons & 2\text{ vol.} \end{array}$$

A change in pressure will not affect the equilibrium state because there is no change in volume when the reaction takes place. Higher temperature will displace the equilibrium to the right, *i.e.*, in the direction of the endothermic reaction. Thus, the yield of nitric oxide is not affected by pressure and is enhanced at higher temperatures.

(4) **Oxidation of carbon monoxide by steam** (*Bosch process*). This reaction is an *exothermic*, reversible reaction, which takes place with no change in volume.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) + x\text{ cal.}$$

Again, altering the pressure will not affect the position of equilibrium. Raising the temperature will displace the equilibrium in the direction of the endothermic reaction, *i.e.*, to the left; lowering the temperature will shift it to the right. Also, addition of steam to the system in equilibrium will cause it to shift to the right. Thus, the optimum conditions for the highest yield of hydrogen are : (*i*) *low temperature* and (*ii*) *a large excess of steam.*

**10·2. Limitations of Le Chatelier's principle.** Le Chatelier's principle is certainly valuable as a means of predicting optimum conditions for the highest yield of a desired product. However, it is not concerned at all with the factors governing the rate at which that yield is obtained. Hence, the guidance offered by Le Chatelier's principle has often to be modified in practice. For example, although the formation of ammonia (reaction 1 above) by the combination of nitrogen and hydrogen is favoured by a low temperature according to Le Chatelier's principle, the operating temperature in the Haber's process is about 500°C. This is because at lower temperatures the combination of nitrogen and hydrogen occurs extremely slowly, even in the presence of catalyst. Hence, exothermic processes are operated at such lowest temperatures at which neither the yield of the desired product will be very low nor the rate of reaction be too slow. This is why the contact process (reaction 2 above) and Bosch process (reaction 3 above) are operated around 450-500°C.

**10-3. Applications of Le Chatelier's principle to physical equilibria**. Le Chatelier's principle is equally applicable to physical equilibria such as—

(1) *Melting of ice.* Ice melts with absorption of heat and decrease in volume :

$$\underset{\text{(more volume)}}{\text{Ice}} \rightleftharpoons \underset{\text{(less volume)}}{\text{Water}} - x \text{ cal.}$$

Hence, raising the temperature and increasing the pressure favour the change of ice into water. The reverse change, *i.e.*, freezing of water to ice is favoured by lowering the temperature as well as the pressure.

(2) *Vaporization of water.* Water evaporates with absorption of heat and increase in volume.

$$\underset{\text{(less volume)}}{\text{Water}} \rightleftharpoons \underset{\text{(more volume)}}{\text{Water vapour}} - x \text{ cal.}$$

Thus, vaporization of water is favoured by raising the temperature and lowering the pressure; change of water vapour into liquid water is favoured by lowering the temperature and increasing the pressure.

(3) *Solubility of substances* Consider a physical equilibrium between a saturated solution and excess of undissolved solute. If the solute dissolves with absorption of heat, rise in temperature will cause more of it to dissolve so that the temperature is lowered again. That is, the solubility of such a solid will increase with rise in temperature.

$KCl + aq \rightarrow KCl(aq) - x$ cal. (*solubility rises with temp.*)
Solubilities of such substances as KOH etc., decreases upon raising the temperatures because they dissolve with evolution of heat.

$KOH + aq \rightarrow KOH(aq) + x$ cal. (*solubility decreases with temperature*).

## 11. Calculations Involving Equilibrium Constants

**Example 1.** *10 moles of HI were produced by the interaction of 15 moles of* $H_2$ *and 5·2 moles of* $I_2$ *vapour at 444°C. Calculate the equilibrium constant of the reaction* $H_2 + I_2 \rightleftharpoons 2HI$.

**Solution.** If $2x$ moles of HI are formed in the reaction, the system in question may be represented as

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

| | | | |
|---|---|---|---|
| **Initial concentration (mole/$l$) :** | $a$ | $b$ | $o$ |
| **Equilibrium concentration (mole/$l$) :** | $(a-x)$ | $(b-x)$ | $2x$ |

According to the data,

$$a = 15 \text{ moles}, \ b = 5\cdot2 \text{ moles}$$
$$2x = 10 \text{ moles} \ ; \ \therefore \ x = 5 \text{ moles}$$

Hence, $[HI] = 10$ moles

$$[H_2] = (a-x) = 15 - 5 = 10 \text{ moles}$$
$$[I_2] = (b-x) = 5\cdot2 - 5 = 0\cdot2 \text{ moles}$$

Substituting these values in the equilibrium constant expression,

$$\frac{[HI]^2}{[H_2]\,[I_2]}$$

$$K_c = \frac{(10 \text{ moles})^2}{10 \text{ mole} \times 0\cdot2 \text{ mole}} = \mathbf{50}$$

**Example 2.** *For the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at a given temperature it is found that an equilibrium mixture in a 10 litre container contains 20 moles of $NH_3$, 0·20 mole of $N_2$, and 6·0 moles of $H_2$. What is the value of the equilibrium constant at this temperature ?*

**Solution.** $K_c = \dfrac{[NH_3]^2}{[N_2]\,[H_2]^3}$

Since these are all molar concentrations, the number of moles of each substance must be divided by the total volume of the container.

$$K_c = \frac{(2\cdot0 \text{ mol}/10\ l)^2}{(0\cdot20 \text{ mol}/10\ l)\,(6\cdot0 \text{ mol}/10\ l)^3}$$
$$= \mathbf{9\cdot3}\ l^2 \text{ mol}^{-2}.$$

**Example 3.** *2 moles of HI were heated in a sealed tube at 444°C till the equilibrium was reached. It was found to be 22 per cent dissociated. Calculate the equilibrium constant for the reaction.*

Since the dissociation of HI ($2HI \rightleftharpoons H_2 + I_2$) occurs to the extent of 22%, the amount of HI dissociated will be $2 \times 22/100 = 0\cdot44$ moles. From the stoichiometry of the reaction, the system may be represented as follows :

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

| | | | |
|---|---|---|---|
| **Initial concentrations (mole/$l$) :** | $2/V$ | 0 | 0 |
| **Equilibrium concentrations (mol/$l$) :** | $(2-0\cdot44)/V$ | $0\cdot22/V$ | $0\cdot22/V$ |

($\because$ 1 mol of HI gives on dissociation $\frac{1}{2}$ mole of $H_2$ and $\frac{1}{2}$ mole of $I_2$. V is the volume of the sealed tube in litres).

$$\text{Equilibrium constant, } K=\frac{[H_2]\,[I_2]}{[HI]^2}$$

$$=\frac{\dfrac{0{\cdot}22}{V}\times\dfrac{0{\cdot}22}{V}}{\dfrac{1{\cdot}56}{V}\times\dfrac{1{\cdot}56}{V}}$$

$$=\frac{0{\cdot}22\times0{\cdot}22}{1{\cdot}56\times1{\cdot}56}=\mathbf{0{\cdot}0199}\text{ at }440°C$$

**Example 4.** *The value of $K_c$ for the reaction $A + B \rightleftharpoons C + D$ is 2. Calculate the concentrations of A, B, C, and D at equilibrium if the initial concentrations of A and B were $[A]=5$ moles per litre; $[B]=2$ moles per litre.*

It is clear from the equation of the reaction that 1 mole of C and 1 mole of D are formed from each mole of A and B. Let the number of moles of A and B that have been transformed into C and D be $x$. Then the initial and equilibrium concentration of A, B, C, and D are :

| | A + | B ⇌ | C + | D |
|---|---|---|---|---|
| **Initial concentration (mol/l) :** | 5 | 2 | 0 | 0 |
| **Equilibrium concentration (mol/l) :** | $(5-x)$ | $(2-x)$ | $x$ | $x$ |

Substituting these values in the equilibrium constant expression,

$$2=\frac{x\times x}{(5-x)\,(2-x)};\quad x^2-14x+20=0$$

$$\text{or}\qquad x_1=12{\cdot}39,\ x_2=1{\cdot}61$$

Discarding the first root as impossible, the concentrations at equilibrium are : $[C]=[D]=1{\cdot}61$ moles per litre; $[A]=3{\cdot}39$ moles per litre, and $[B]=0{\cdot}39$ moles per litre.

## Questions

1. Arrange the following reactions in two groups, fast and slow, basing your answer on the chemical bonds involved in tee process :

(*a*) $C + O_2 \rightarrow CO_2$

(*b*) $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$

(*c*) $H^+ + OOC.CH_3^- \rightarrow CH_3.COOH$

(*d*) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

(*e*) $2H^+ + CO_3^{2-} \rightarrow H_2O + CO_2\uparrow$

(*f*) $CH_3.COOH + C_2H_5OH \rightarrow CH_3.COOC_2H_5 + H_2O$

2. How is the rate of reaction expressed quantitatively ? Explain by means of a suitable example.

3. Define or explain each of the following terms :

(1) reaction rate (2) activation energy

(3) catalyst (4) inhibitor

(5) reversible reaction (6) chemical equilibrium

(7) equilibrium constant (8) Le Chatelier's principle

4. Give a brief account of the collision theory of reaction rate.

5. Explain in terms of collision theory and activation energy, how each of the following factors affects the rate of a chemical reaction :

(*i*) increase in concentration,

(*ii*) increase in temperature, and

(*iii*) the presence of a catalyst.

6. In the reaction between marble and dilute hydrochloric acid, how is the rate of reaction affected by the size of the marble particles ? Explain your answer.

7. Explain why the chemical reactions between ions are very fast while those involving covalently bonded molecules are very slow.

8. Explain the terms : *activated complex*, *energy barrier*, and *activation energy*.

9. Why should increased pressure increase the rate of gaseous reactions only ?

10. How can reactions be speeded up ? (*a*) Between a solid and a gas ? (*b*) A solid and a liquid ?

11. State the law of mass action. How is the speed of the reaction $A + 2B \rightarrow C + D$ affected by (*a*) doubling the concentration of A, (*b*) doubling the concentration of B ?

12. Why is it that the reaction rate is proportional to the mathematical *product* of the concentrations of the reacting substances and not to the mathematical *sum* of their concentrations ?

13. (*a*) Explain the action of a catalyst in increasing the reaction rates.

(*b*) Define with examples the terms 'homogeneous catalysis' and 'heterogeneous catalysis'.

(*c*) Why is the activity of contact catalysts enhanced with their subdivision.

14. Distinguish between *reversible* and *irreversible* reactions giving two examples of each.

15. Why does the reaction between iron and hydrochloric acid proceed to completion although under proper conditions hydrogen reacts with the ferrous chloride formed ?

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$

16. Why is the state of chemical equilibrium referred to as "dynamic" ?

17. Explain the statement that "in a reversible chemical reaction (*e.g.*, $A + B \rightleftharpoons C + D$) the same equilibrium can be attained from either side".

18. (*a*) What is meant by a 'closed system' as applied to an equilibrium state ?

(*b*) The reaction between iron and steam is reversible. Steam passed over a red-hot iron produces iron (II, III) oxide and hydrogen; hydrogen passed over red-hot iron (II, III) oxide gives iron and steam. Suggest a method by which this reversible reaction may be brought to a state of equilibrium.

19. What do you understand by the term 'shift of equilibrium' ? List the factors that may cause a shift of equilibrium in a reversible reaction involving gases.

20. (*a*) When do changes in pressure affect systems in equilibria ?

(*b*) How will an increase in pressure affect the following equilibria ?

*i.* $N_2 + 3H_2 \rightleftharpoons 2NH_2$ + heat

*ii.* $N_2O_4$ + heat $\rightleftharpoons 2NO_2$

*iii.* $3O_2$ + heat $\rightleftharpoons 2O_3$

*iv.* $2CO + O_2 \rightleftharpoons 2CO_2$ + heat

*v.* $CaCO_3$ + heat $\rightleftharpoons CaO + CO_2$

*vi.* $2HI$ + heat $\rightleftharpoons H_2 + I_2$

*vii.* $CO + 2H_2 \rightleftharpoons CH_3OH$ (g) + heat.

21. How will an increase in temperature affect the above equilibria ?

22. Derive the algebraic expressions for the equilibrium constants K*c* and K*p* using the hypothetical equation $mA + nB \rightleftharpoons pC + qD$. Does the value of these constants depend upon concentrations ? Upon temperature ?

23. How does the presence of a catalyst affect (*a*) the rate at which equilibrium is attained, (*b*) the value of the equilibrium constant ?

24. Discuss the significance of the equilibrium constant, *Kc* for reversible reactions.

25. (*a*) State clearly the Le Chatelier's principle.

(*b*) List five ways by which the reversible reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + \text{heat}$$

could be shifted towards the left.

26. Mention three examples of dynamic physical equilibrium and apply Le Chatelier's principle to each one.

27. The reaction between hydrogen and chlorine to form hydrogen chloride is represented by the following equation :

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g) + 44{\cdot}0 \text{ kcal}$$

(*a*) List four important pieces of information regarding the reaction conveyed by this equation.

(*b*) What are the three significant areas of interest concerning this reaction for which no information is conveyed by this equation ?

28. Consider the reversible rection represented by the equation :

$$4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g) + 27 \text{ kcal}$$

How would the equilibrium concentration of $Cl_2$ be affected by the following changes ? Give reasons for each answer.

(*a*) Increasing the concentration of $O_2$.

(*b*) Decreasing the total pressure.

(*c*) Increasing the temperature.

(*d*) Adding a catalyst.

(*e*) Increasing the volume of the reaction chamber.

29. Consider the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3 + x \text{ cal}$$

(*i*) Write down the expression for the equilibrium constants Kc and K*p*.

(*ii*) What is the catalyst used in this reaction ?

(*iii*) Is this catalyst homogeneous or heterogeneous ?

(*iv*) If solid catalysts are used, in what state are they used ?

(*v*) Why are they used in this state ?

30. In the manufacture of ammonia, the reaction is denoted by the following equations :

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + x \text{ kcal}$$

Or, $$N_2 + 3H_2 \rightleftharpoons 2NH_3 \; ; \; \Delta H = -x \text{ kcal.}$$

Applying Le Chatelier's principle, what is the effect of increasing

(*i*) temperature,

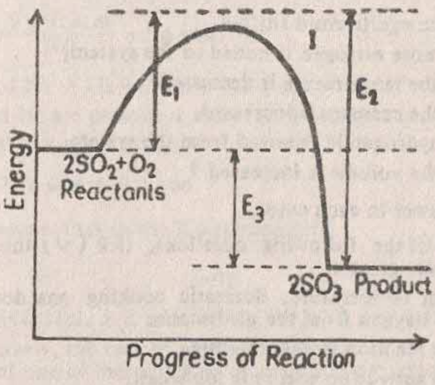
(*ii*) pressure,

(*iii*) volume of hydrogen ?

31. Sulphur trioxide is obtained by the reaction represented by the equation

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The figure below shows the potential energy diagram illustrating the activation energy for the above exothermic reaction.



(*a*) Explain the significance of the energy values $E_1$, $E_2$, and $E_3$.

(*b*) If a catalyst increases the rate of reaction what will be the change in the above diagram if we add a catalyst to the above reaction ? Draw the diagram and label it.

(*c*) Name the catalysts commonly used in this reaction.

(*d*) Is this an example of heterogeneous or homogeneous catalysis according to the choice of catalyst ?

(*e*) Write the equation of equilibrium constant for the reaction using concentration terms.

(*f*) State Le Chatelier's principle.

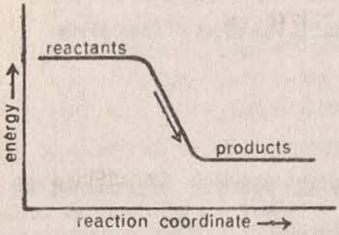
(*g*) Predict the changes in the composition of the equilibrium mixture resulting from—

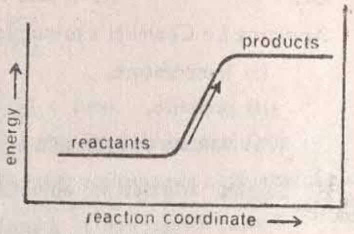
*i*. an increase in total pressure,

*ii*. a rise in temperature, and

*iii*. the removal of some of the $SO_3$

32. (*i*) Which of the following figures (*a*) and (*b*) represent an exothermic reaction ?





(*ii*) Why is an exothermic reaction self-sustaining ?

33. For the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \Delta$$

which way will the equilibrium shift—

(*i*) if more nitrogen is added to the system,
(*ii*) if the temperature is decreased,
(*iii*) if the pressure is increased,
(*iv*) if hydrogen is removed from the system,
(*v*) if the volume is increased ?

Explain your answer in each case.

34. In each of the following questions, tick (√) the correct answer out of the four answers given :

(1) At room temperature, domestic cooking gas does not ignite spontaneously with the oxygen from the air because

A. the reaction is endothermic.
B. the activation energy is too small.
C. the energy of reactants is greater than the energy of the products.
D. the collision energy is unsufficient to overcome the energy barrier.

(2) A catalyst increases the rate of reaction by

A. reducing the energy that the molecules must have before they can react.
B. removing substance that slow down the reaction.
C. raising the energy barrier.
D. lowering the energies of both the reactants and the products.

## Problems

1. Write an expression for the rate of reaction of the combustion of sulphur : $S + O_2 \rightarrow SO_2$. $(R = k[O_2])$

2. Derive the mathematical expression of the Law of Chemical Equilibrium for the following equilibria :

(*i*) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
(*ii*) $CO + 2O_2 \rightleftharpoons CH_3OH(g)$

(*iii*) $CO_2 + H_2 \rightleftharpoons CO + H_2O(g)$

(*iv*) $2SO_2 + O_2 \rightleftharpoons 2SO_3(g)$

**Ans.** (*i*) $Kc = [CO_2]$; (*ii*) $Kc = \dfrac{[CH_3OH]}{[CO]\,[H_2]^2}$

(*iii*) $Kc = \dfrac{[CO][H_2O]}{[CO_2][H_2]}$; (*iv*) $Kc = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

3. For the reaction $2A(g) + B(g) \rightleftharpoons 2C(g)$, $Kc = 0{\cdot}18$ at 200°C. Calculate

(*a*) Kc for the reaction $2C(g) \rightleftharpoons 2A(g) + B(g)$

(*b*) Kc for the reaction $4A(g) + 2B(g) \rightleftharpoons 4C(g)$

[**Ans.** (*a*) 5·55..., (*b*) 0·0324]

4. It was found that a mixture of nitrogen and hydrogen in the proportion of 1 : 3 by volume and under a pressure of 40 atmospheres and temperature 450°C gave on equilibrium mixture containing 6% ammonia, Calculate the equilibrium constant. [**Ans.** 0·0053]

[**Hint.** $Kp = \dfrac{P_{NH_3}}{P_{N_2}{}^{\frac{1}{2}} \times P_{H_2}{}^{\frac{3}{2}}}$ $(\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3)$

$P_{NH_3} = \dfrac{6 \times 40 \text{ atm}}{100} = 2{\cdot}4$ atm.

$\therefore$ Pressure of $N_2 + H_2 = 40 - 2{\cdot}4 = 37{\cdot}6$ atm,

Since $N_2$ and $H_2$ are present in the proportion 1 : 3

$P_{N_2} = \frac{1}{4} \times 37{\cdot}6 \text{ atm} = 9{\cdot}4$ atm.

and, $P_{H_2} = \frac{3}{4} \times 37{\cdot}6 \text{ atm} = 28{\cdot}2$ atm.

Substitute these values in the Kp expression.]

## Key

1. Reactions (*b*), (*c*), and (*e*) are fast; (*a*), (*d*), and (*f*) are slow.

2. Quantitatively, the rate of reaction is expressed in terms of the change in concentration of one of the reactants or products per unit time.

9. The rate of reaction is proportional to the concentration (in moles per litre) of the reactants. It is in the case of gaseous reactions only that increased pressure results in increased concentration of the reactants so that the rate of reaction is also increased.

10. (*a*) By (*i*) bringing the solid in a finely divided state, (*ii*) increasing the pressure; (*iii*) increasing the temperature, and (*iv*) using a suitable catalyst.

(*b*) By (*i*) bringing the solid in a finely divided state, (*ii*) increasing the temperature, and (*iii*) using a suitable catalyst.

11. (*a*) The speed is doubled. (*b*) The speed is quadrupled.

15. Because the hydrogen formed leaves the system as it is formed, and so the reaction continues to proceed in the forward direction.

16. The state of chemical equilibrium is referred to as dynamic because it is the result of two opposite reactions proceeding at equal rates and not of their ceasing to occur.

18. (*b*) The reversible reaction between iron and steam may be brought to a state of equilibrium by carrying it in a closed vessel so that the hydrogen or steam may not leave the system.

20. (*a*) Changes in pressure affect systems in equilibria when gases are involved and the chemical reaction involves a change in the total number of molecules in the system.

(*b*) Shift towards right in (*i*), (*iii*), (*iv*), and (*vii*).
Shift towards left in (*ii*) and (*v*).
No change in (*vi*).

25. (*b*) 1. By decreasing the concentration of $N_2$.
2. By decreasing the concentration of $H_2$.
3. By increasing the concentration of $NH_3$.
4. By increasing the temperature.
5. By decreasing the pressure.

26. Examples of dynamic physical equilibria are :

(1) Melting of ice, (2) Vaporization of water, and (3) A saturated solution in contact with undissolved solute.

See page 172 for the application of Le Chatelier's principle to these equilibria.

27. (*a*) (1) The reaction is reversible.

(2) Increase in temperature will decrease the yield of HCl since the forward reaction is exothermic.

(3) Decrease in temperature will increase the yield of HCl as its formation is accompanied with liberation of heat.

(4) The yield of HCl is not affected by a change in pressure since there is no change in the total number of molecules in the system.

(*b*) (1) The extent to which the reaction proceeds when the equilibrium is attained.

(2) The rate of attainment of equilibrium.

(3) The catalyst for the forward reaction.

28. (*a*) Increases ; since this will favour the forward reaction in which $O_2$ is used up and its concentration is decreased.

(*b*) Decreases; since this will shift the equilibrium to the direction in which the volume is more, *i.e.*, to the left.

(*c*) Decreases; since the forward reaction is accompanied with liberation of heat.

(*d*) No change; since catalyst does not affect equilibrium concentrations.

(*e*) Decreases; since this is equivalent to reducing the pressure.

29. (*i*) $Kc = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$ ; $Kp = \frac{P_{SO_3}{}^2}{P_{SO_2}{}^2 \times P_{O_2}}$

(*ii*) Finely divided platinum (deposited on asbestos or magnesium sulphate) or vanadium pentoxide.

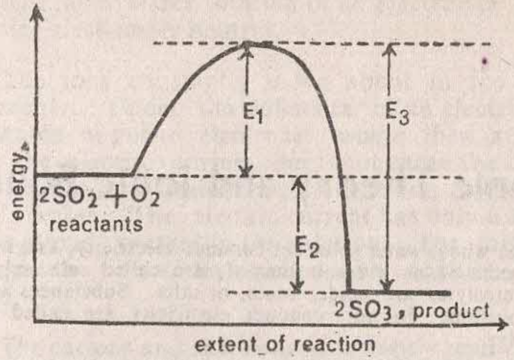
(*iii*) Heterogeneous

(*iv*) In a very finely divided state.

(*v*) To provide maximum surface for the adsorption of reacting molecules whereby the energy of activation is lowered and the frequency of collisions is increased.

31. (*a*) $E_1$ is the activation energy for the reaction; $E_3$ is difference in energy of the activated complex and sulphur trioxide, the product. and $E_2$ is the energy released in the reaction.

(*b*) The hump of the curve will be lowered as shown in the diagram below :



(*d*) Yes ; it will be an example of homogeneous catalysis if oxides of nitrogen (gaseous) are used as catalyst, and of heterogeneous catalysis if platinum or vanadium pentoxide is used as catalyst.

(*g*) (*i*) The equilibrium concentration of $SO_3$ will increase; of $SO_2$ and $O_2$ will decrease.

(*ii*) The equilibrium concentration of $SO_3$ will decrease; of $SO_2$ and $O_2$ will increase.

(*iii*) The concentrations of $SO_2$ and $O_2$ will increase.

32. (*a*) Fig. (*a*) represents an exothermic reaction.

33. (*i*) Equilibrium will shift to the right (to use up additional nitrogen).

(*ii*) Equilibrium will shift to the right (since this is an exothermic reaction where heat can be thought of as a product; decreasing the temperature is equivalent to removal of heat).

(*iii*) Equilibrium will shift to the right (since the pressure is lower on the right side corresponding to the smaller number of moles).

(*iv*) Equilibrium will shift to the left (since ammonia will decompose to maintain the value of equilibrium constant $Kc = [NH_3]^2/[N_2][H_2]^3$.

(*v*) Equilibrium will shift to the left (increasing the volume means decreasing the pressure; pressure is more on the left side corresponding to the larger number of moles).

34. (1) D, (2) A.

□

# 7

# Ionic Theory and Ionic Equilibria

Substances whose water solutions conduct electricity, and which are decomposed as a result thereof, are called **electrolytes**. Most electrolytes are acids, bases, or salts. Substances whose water solutions do not conduct electricity are called **non-electrolytes.**

Electrolytes differ from non-electrolytes not only in the matter of electrolytic conduction in water solutions, they also affect the freezing point, boiling point, and osmotic pressure to a much greater extent than do the non-electrolytes. Thus, one mole of sodium chloride dissolved in 1 kg of water lowers the freezing point of water 3·42°C; one mole of sugar dissolved in 1 kg of water lowers the freezing point of water 1·86°C. Similarly, electrolytes in water solutions raise the boiling point nearly 2, 3, or more times as much as the non-electrolytes of the same molality.

To explain the behaviour of electrolytes in water solutions, Arrhenius, a Swedish chemist, in 1887 proposed a theory called the '*theory of electrolytic dissociation*', or the '*ionic theory*'. This theory successfully explains why electrolytes give solutions which conduct an electric current and affect the freezing point, boiling point, and osmotic pressure more than do the non-electrolytes.

Although Arrhenius' ionic theory has since been modified in the light of our present knowledge of atomic structure and chemical bonding, the modern theory of electrolytes incorporates most of the principal postulates of the Arrhenius theory.

## 1. The Ionic Theory

To account for the differences between the solutions of electrolytes and non-electrolytes, Arrhenius in 1887 proposed a theory called the ionic theory. The main points of this theory are :

(1) Molecules* of electrolytes break down into two or more *ions* in solution. An ion may be defined as an atom or a group of atoms carrying a net charge which is numerically equal to the valency number of the element or radical. Each substance forms two kinds of ions, carrying positive and negative charges respectively.

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*It may be noted that it is not appropriate to speak of 'molecules' of completely ionic compounds; the term *molecule* should be used only for predominantly covalent substances.

(2) The sum of the electrical charges on the positive ions or *cations* equals the sum of the electrical charges on the negative ions or *anions* in the water solution of an electrolyte which, therefore, remains electrically neutral.

(3) The ions constantly move about in the solution* in a random manner. Under the influence of an electric current they travel towards opposite electrodes where they are discharged. However, the electric current does not cause the decomposition of molecules into ions which occurs as soon as the electrolyte is dissolved in water. The electric current has only a *directive* effect on the ions already present in the solution. The migration of the ions towards the eletrodes makes the solution an electrical conductor.

(4) The cations and anions are constantly reuniting in solution to form undissociated molecules. Thus, there exists a *dynamic equilibrium* between the undissociated molecules and the ions. The equilibrium existing in a solution of sodium chloride may be represented thus,

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

(5) Dissociation into ions is never complete except in very dilute solutions. The ratio of the number of dissociated molecules to the total number of molecules in solution is called the 'degree of dissociation' of an electrolyte.

**1-1. Dissociation of electrolytes.** Polyprotic acids, *i.e.*, acids that have more than one ionizable hydrogen, dissociate by steps. Thus, sulphuric acid first dissociates according to the equation

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

The second hydrogen ion splits off according to the equation

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

with much greater difficulty as it has to overcome the attractive force of the doubly charged $SO_4^{2-}$ ion. It must be realized, therefore, that the equation

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

is fictitious as it implies that sulphuric acid dissociates in one step. However, such equations are used in qualitative discussions.

Phosphoric acid, $H_3PO_4$, dissociates in three steps :

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$
$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$$
$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$$

---

*The term ion has been derived from a Greek word meaning 'wanderer' or 'traveller'.

Bases containing more than one hydroxyl radical in their molecules also dissociate by steps. For example,

$$Ca(OH)_2 \rightarrow Ca(OH)^+ + OH^-$$

$$Ca(OH)^+ \rightarrow Ca^{2+} + OH^-$$

*Normal* salts dissociate into the metal ions and the ions of the acid radicals. For example,

$$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$$
$$MgCl_2 \rightleftharpoons Mg^{2+} + 2Cl^-$$

*Acid salts*, however, like polyprotic acids, dissociate by steps. For example,

$$NaHSO_4 \rightleftharpoons Na^+ + HSO_4^-$$
$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

**1-2. The hydronium ion.** The hydrogen ion, $H^+$, is actually a proton, and does not exist free in water solutions. It exists as the hydrated ion, $H_3O^+$,$(H^+H_2O)$, called the *hydronium ion* which is produced by the interaction of the acid and water. Thus, in the case of hydrochloric acid,

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

Chemically, the hydronium ion, $H_3O^+$, acts just like a hydrogen ion, and in any reaction involving the hydronium ion the water of hydration is always left behind. For convenience, therefore, $H_3O^+$ is represented as $H^+$ in the dissociation equations.

## 2. Evidence in Favour of Ionic Theory

**2-1. Direct evidence.** Direct evidence in favour of the ionic theory comes from the following studies :

(1) *X-ray diffraction studies.* X-ray diffraction studies of solid salts show that these are built up of ions arranged in a regular pattern, and not of molecules. However, since the crystal lattice restricts the movement of ions, the solid crystals are not good conductors of electricity. When a salt is fused or dissolved in an ionizing solvent, the constituent ions become free to move about. This is why the melts or solutions of electrolytes conduct an electic current.

(2) *Appearance of charges in the electrolyte solutions.* A sealed tube containing a solution of silver nitrate, $AgNO_3$, is clamped to a disc that can be rotated. The tube has platinum wires fused at both ends which are connected by a special device to a sensitive voltmeter. When the disc is rotated at a high speed, the indicator of the voltmeter deflects perceptibly showing the presence of unlike charges at the two electrodes. The end of the tube nearer the edge of the disc is charged positively while that

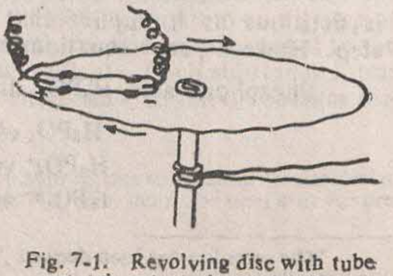

Fig. 7-1. Revolving disc with tube containing electrolyte solution.

nearer the centre is charged negatively. This is because the heavier, positively charged silver ions are thrown outwards with a greater force and, therefore, to a greater distance from the axis of rotation than the lighter nitrate ions, which carry negative charge. Thus, there is an accumulation of the positive silver ions towards the edge end and of the negative nitrate ions towards the centre end of the tube.

If the same experiment is performed with a solution of potassium iodide, KI, the edge end of the tube will be charged negatively owing to the accumulation of the heavier, negative iodide ions, and the centre end positively.

**2-2. Indirect evidence.** The indirect evidence in support of the ionic theory comes from the explanations it offers for the following facts :

(1) *Electrical conductivity of acid, base, and salt solutions.* The solutions of acids, bases, and salts contain electrically charged positive and negative ions. Under the influence of an electric field these ions bodily move through the solution towards the electrode of opposite charge. At the electrodes a process of discharge occurs. At the negative electrode, where there is a surplus of electrons, the positive ions pick up enough electrons to become neutral atoms. At the positive electrode, where there is a shortage of electrons, the negative ions give up their surplus electrons to become neutral atoms (or radicals) at the same rate that the positive ions are picking them up at the negative electrode. Thus, the electrons continue to flow through the external circuit as readily as though the electrodes had been connected with a connecting wire. The net effect is the conduction of electric current across the electrodes although no current actually passes through the solution.

(2) *Large increase in osmotic pressure, freezing point lowering, and boiling point rise of solutions of electrolytes.* Solutions of electrolytes exert higher osmotic pressures and show larger depressions of freezing point or elevation of boiling point than might be expected on consideration of their molecular weights. The reason is that these properties are directly proportional to the number of particles of solute present (hence, these are known as *colligative* properties). Electrolytes affect the osmotic pressure and the freezing and boiling points abnormally because their molecules dissociate into ions, each ion having the same colligative effect as an undissociated molecule. A 1-molal solution* of any covalent solute in a given solvent exerts the same osmotic pressure, and gives a constant lowering in freezing point and rise in boiling point because 1 mole of any covalent substance always contains the same number of molecules, *viz.*, $6{\cdot}02 \times 10^{23}$, and in 1000 grams of any solvent the number of solvent molecules will also be constant. On the other hand, a 1-molal solution of an electrolyte contains a much large number of particles owing to dissociation of molecules into

---

**Molality* of a solution is defined as the *number of moles of solute per 1000 grams of the solvent*. A 1-molal solution contains 1 mole of the solute dissolved in 1000 grams of the solvent.

ions. Since, different solutes dissociate to different extent, equimolal solutions of different electrolytes cause different rise in boiling point or depression in freezing point.

(3) *Common properties shown by similar compounds.* All copper (II) salts form blue solutions in water which upon electrolysis give a deposit of metallic copper on the cathode. This is because all copper (II) salts, *e.g*, copper (II) sulphate, copper (II) chloride, etc., contain copper (II) ion, $Cu^{2+}$. Similarly, solutions of all iron (II) salts give deep blue precipitate with potassium ferrocyanide solution as they all contain the iron (II) ion, $Fe^{2+}$. Indicators are affected in the same way by all acid or all base solutions since they furnish the common $H^+$ ions or $OH^-$ ions respectively to the solution. It is the common $H^+$ ion or $OH^-$ ion rather than the entire acid or base which affects the colour of the indicator.

(4) *High speed of reactions between solutions of electrolytes.* The electrolytes, *i.e.*, acids, bases, or salts, dissociate into ions as soon as they dissolve. When solutions of different electrolytes are mixed, oppositely charged ions interact instantaneously because of their mutual electrical attraction. In general, such reactions occur when—

(*a*) One of the products is only sparingly soluble and separates as a precipitate, *e.g.*, reaction between $AgNO_3$ and HCl.

$$\underset{\text{(from AgNO}_3\text{)}}{Ag^+ + NO_3^-} + \underset{\text{(from HCl)}}{H^+ + Cl^-} \longrightarrow AgCl\downarrow + H^+ + NO_3^-$$

(*b*) One of the products is only slightly dissociated, *e.g.*, water in the neutralization reactions of acids and bases.

$$\underset{\text{(from NaOH)}}{Na^+ + OH^-} + \underset{\text{(from HCl)}}{H^+ + Cl^-} \longrightarrow Na^+ + Cl^- + \underset{\text{(slightly dissociated)}}{H_2O}$$

(*c*) One of the products is volatile and escapes as a gas, *e.g.*, $H_2S$ in the reaction between FeS and $H_2SO_4$.

$$\underset{\text{(from FeS)}}{Fe^{2+} + S^{2-}} + \underset{\text{(from H}_2\text{SO}_4\text{)}}{2H^+ + SO_4^{2-}} \longrightarrow Fe^{2+} + SO_4^{2-} + H_2S\uparrow$$

## 3. Ions and Atoms

An ion is formed when an atom either gains or loses 1, 2, or 3 electrons. It, therefore, contains as many electrons fewer or more than the corresponding atom. The main points of difference between ions on the one hand and neutral atoms on the other are :

(1) *Electrical charge.* The atom is electrically neutral; the ion formed from it is electrically charged—positive if it is formed by the loss of electrons, negative if it is formed by the gain of electrons.

(2) *Existence.* An ion has an independent existence in solution; an atom may or may not be capable of independent existence. Sodium ions exist independently in water solutions of sodium salts; sodium atoms cannot exist in water and react with it to form sodium hydroxide and hydrogen.

(3) *Properties.* The properties of ions are absolutely different from those of the corresponding atoms (or groups of atoms, *i.e.*, radicals). For example, hydrogen-ion can be obtained in solution in very large quantities and affects indicators, hydrogen gas is insoluble in water and has no effect on indicators; chloride-ion has neither the colour, odour, nor any of the other properties of chlorine gas; $NO_3^-$ ion can exist only in solution, and only while it is negatively charged, no neutral molecules of such a composition exist, and the same is true of all other compound radicals.

## 4. Dissociation and Ionization

Electrovalent compounds are composed of ions that break away from their crystal lattice when dissolved in water by hydration process. This process is called electrolytic dissociation or simply *dissociation* and the compound is said to dissociate in water. Thus, when sodium chloride is dissolved in water, the constituent $Na^+$ and $Cl^-$ ions separate and become distributed independently in the solution.

$$\underset{\text{crystalline}}{Na^+Cl^-} \xrightarrow[\text{dissociation}]{H_2O} Na^+ + Cl^-$$

Thus, dissociation results, not in the formation of ions, but in the separation of ions and their becoming independent of each other.

Non-ionic electrolytes consisting of highly polar molecules form ions by reacting with water. The water dipoles attracted to the ends of the polar covalent molecule stretch the latter, moving its poles apart. As a result, the polar molecule breaks up into separate ions as their hydrates (Fig. 7-2). Since the ions did not exist in the undissolved solute, but were formed by reaction with water, the process is called *ionization*.

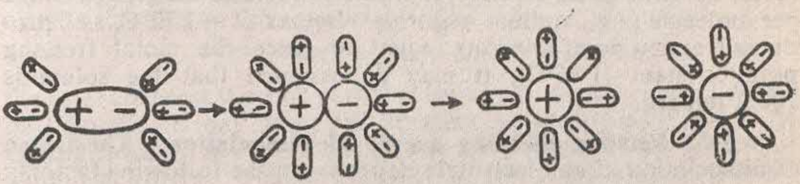

Fig. 7-2. Ionization of polar covalent molecules in solution.

The ionization of hydrogen chloride, for example, can be explained as follows :

Hydrogen chloride molecules consist of hydrogen and chlorine atoms connected by a shared pair of electrons, *i.e.*, a covalent bond. However, the more highly electronegative chlorine atom attracts the electrons forming the covalent bond causing the chlorine end of the molecule to become negative and the hydrogen end to become positive. The magnitude of the charge on these atoms is much less than of the charge on the ions and is denoted as $-\delta$ and $+\delta$ respectively. When hydrogen chloride is dissolved in water, chlorine atom separates as chloride ion with both the shared electrons. The hydrogen atom, deprived of its lone electron, separates as the hydrated ion, $H_3O^+$, called the *hydronium ion* (Fig. 14-3).

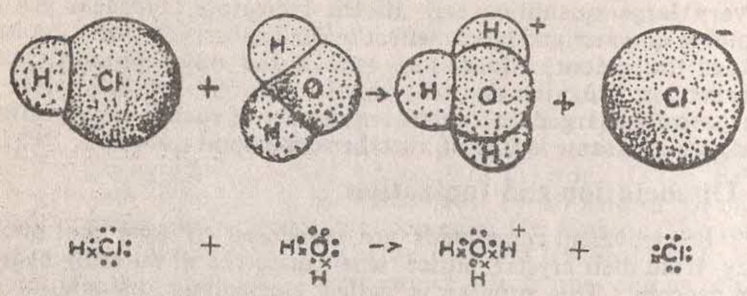

Fig. 7-3. The polar hydrogen chloride molecule ionizes in water solution to form the hydronium ion, $H_3O^+$, and the chloride ion, $Cl^-$.

## 5. Degree of Dissociation

**5-1. Measurement of degree of dissociation.** The electrical conductivity of an electrolyte solution is directly proportional to the number of ions in a given volume of it; the larger the number of ions the better a conductor of electricity it will be, and *vice versa*. The number of ions in the solution depends on the degree of dissociation of the solute. Hence, the electrical conductivity of an electrolyte solution is a measure of the degree of dissociation of the electrolyte. The degree of dissociation can thus be measured by measuring the electfical conductivity.

The degree of dissociation can also be determined by measuring the lowering of the freezing point (or elevation of the boiling point) caused by an electrolyte in a known quantity of solvent. If molal solution of an electrolyte which dissociates to give two ions per molecule (*e.g.*, sodium chloride) freezes at −3·72°C, *i e.*, produces freezing point lowering equal to twice the molal freezing point constant (1·86°C), it may be assumed that the solute is 100% ionized.

**5-2. Factors affecting degree of dissociation.** The degree of dissociation of an electrolyte depends on the following factors :

(1) *Nature of the solute.* Ionic compounds dissociate almost completely in water solutions, and are called *strong electrolytes.* Compounds with only a slight amount of ionic character dissociate only to a small extent, and are called *weak electrolytes*. Mineral acids, alkalis, and most of the salts are strong electrolytes. Organic acids (*e.g.*, acetic acid), some bases such as ammonium hydroxide, and a very few salts belong to the class of weak electrolytes.

(2) *Nature of solvent.* Solvents with high dielectric constants are highly ionizing while those with low dielectric constants are poorly ionizing. The highest dielectric constant among ordinary

solvent is that of water, 81, which is at the same time the best ionizing solvent. Formic acid, ethyl alcohol, and acetone are examples of other ionizing solvents. Their molecules, like those of water are distinctly polar. Non-polar or slightly polar solvents, such as benzene, ether, chloroform, etc., have low dielectric constants. In such solvents ionization does not occur. The same substance may behave as a strong electrolyte in an ionizing solvent and as a weak electrolyte in a non-polar solvent, or *vice versa*. Thus, hydrochloric acid is a strong electrolyte in water but a very weak electrolyte in organic solvents.

(3) *Effect of other solvents*. The degree of dissociation of weak electrolytes is suppressed by the presence of a solute which gives a common ion For example, the degree of dissociation of ammonium hydroxide is lowered in the presence of ammonium chloride, which gives the common $NH_4^+$ ion.

(4) *Concentration*. The degree of ionization of electrolytes, especially the weak electrolytes, increases with dilution; *i.e.*, with increase in volume of the solvent for a given weight of the electrolyte. Ionization is almost complete at very high dilutions (*Infinite dilution*).

(5) *Temperature*. In general, the degree of dissociation increases with rise in temperature.

## 6. The Interionic Attraction Theory

A 1-molal solution of sodium chloride in water freezes at —3·42°C. That is, the freezing point lowering of 1-molal NaCl is 3·42°C. The molal freezing point constant of water being 1·86°C, the increase in lowering produced by 1-molal NaCl is 1·56°C, or about 84 per cent. Similarly, for the rise in boiling point, the increase is about 88 per cent. However, if NaCl completely dissociated according to the equation,

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

the total concentration of particles (ions) in 1-molal NaCl would be 2-molal. In that case, the freezing point lowering should be exactly twice as much as that caused by 1-molal concentration of a non-electrolyte That is, the freezing point lowering of 1-molal NaCl should be 2×1·86°C or 3·72°C instead of 3 42°C.

In general, the freezing point lowering or boiling point rise of molal solutions of strong electrolytes is never quite as large as that calculated for complete dissociation. Arrhenius accounted for this discrepancy between calculated and observed values for the colligative properties of solutions of electrolytes by postulating that electrolytes never completely dissociate, and that a certain percentage remains in molecular form. In 1-molal NaCl at its freezing point, for example, the salt is dissociated to the extent of 84 per cent. Then, for every 100 'molecules' in solution, there are formed 184 particles (2×84=168 ions and 16 undissociated molecules).

Such a solution would therefore lower the freezing point of water only 1 84 times instead of 2 times the molal depression for a solute which does not dissociate. Similarly, it was argued that 1-molal solution of NaCl was 12 per cent molecular and 88 per cent ionic at its boiling point, which accounted for the 88 per cent rise in boiling point.

The postulate of the incomplete dissociation of strong electrolytes is no longer held true. X-ray evidence is convincing that most such compounds are already completely ionized, even in their solid state. Hence, by the very nature of their structure, they must be completely ionized in solution. The apparent lack of complete dissociation in such solutions is attributed to the electrical forces between the ions in solution. According to this view, known as the **interionic attraction theory** of Debye and Huckel, the attraction between ions of opposite charge prevents them from behaving as totally independent particles, especially in concentrated solutions. Charged ions, when close together in solution, alter each other's effectiveness or *activity* as independent units. Some of the ions tend to act as a group rather than as individual particles. In this way the *apparent* number of ions is smaller than the actual number. The colligative properties will be influenced accordingly. The more dilute the solution, the farther apart the oppositely charged ions and the less the interionic attraction. Thus, the *apparent degree of dissociation* increases with dilution. Water solutions of various concentrations of sodium chloride, for example, give the molal freezing point lowerings shown in Table 14-1.

**Table 14-1** *Molal freezing point lowerings in water solutions of sodium chloride*

| *Concentration of NaCl in water solution* | *Freezing point lowering/mole NaCl, °C* |
|---|---|
| 0·10M | 3·48 |
| 0 010M | 3·60 |
| 0·0010M | 3·66 |
| 0·00,010M | 3·72 |

**6-1. Activity coefficients.** Because of the interionic forces of attraction, the *effective* concentration or activity of the ions is less than the molar concentration of the electrolyte. *The ratio of the activity of an ion to its concentration is called the* **activity coefficient.** The activity coefficient approaches unity with increasing dilution. For many common ions, the activity coefficients range from about 0·9 in 0·01M solutions to about 0·7 in 0 2M solutions. For a 0·1M solution of sodium chloride, the activity coefficient is 0·8; the activity of the ions is 0·8×0·1M, or 0·08M.

## 7. Ionic Equilibria

Strong electrolytes are completely in the ionic condition in aqueous solutions. As such, the ion concentrations in the aqueous solution of a strong electrolyte may be found directly from the molar concentration of the solution. For example, in a 0·001M solution of soddium chloride ($NaCl \rightarrow Na^+ + Cl^-$), the sodium ion concentration, $[Na^+]$, is equal to the chloride ion concentration, $[Cl^-]$, and both concentrations have the value 0·001M, or $1 \times 10^{-3}$M. In a 0·001M solution of sodium sulphate ($Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$), on the other hand, the sodium ion concentration, $[Na^+]$ is $2 \times 0{\cdot}001$M or $2 \times 10^{-2}$M and the sulphate ion concentration, $[SO_4^{2-}]$ is 0·001M or $1 \times 10^{-3}$M. This is because each sodium sulphate molecule dissociates to give two sodium ions but only one sulphate ion.

Solutions of weak electrolytes contain both the free ions and the non-ionized molecules of the electrolyte, and a condition of equilibrium exists between the two. Such an equilibrium may be expressed as

$$AB \rightleftharpoons A^+ + B^-$$

To such a system in equilibrium the law of mass action (Chapter 6) may be applied.

## 8. Ostwald's Dilution Law

Consider a solution containing one mole of weak binary electrolyte *AB* in *V* litres of solution. Let $a$ be the fraction of *AB* dissociated at this dilution, so that the non-dissociated fraction will be $1-\alpha$.

| | $AB$ | $\rightleftharpoons$ | $A^+$ | $+$ | $B^-$ |
|---|---|---|---|---|---|
| Amount present at equilibrium : | $(1-\alpha)$ mole | | $\alpha$ mole | | $\alpha$ mole |
| Concentration at equilibrium : | $\frac{(1-\alpha)}{V}$ mole/$l$ | | $\frac{\alpha}{V}$ mole/$l$ | | $\frac{\alpha}{V}$ mole/$l$ |

Applying the law of mass action,

$$\frac{[A^+][B^-]}{[AB]} = \text{constant, at constant temperature.}$$

Or, substituting the values of $[A^+]$, $[B^-]$, and $[AB]$,

$$\frac{\frac{a}{V} \times \frac{a}{V}}{\frac{(1-a)}{V}} = \frac{a^2}{(1-a)V} = \text{constant, } K \quad \text{(at constant temperature)}$$

The equation $\frac{a^2}{(1-a)V} = K$ expresses the relationship between the degree of dissociation of a weak electrolyte and its dilution, and is the mathematical form of *Ostwald's dilution law*. The constant $K$ is known as the *dissociation constant* of the weak electrolyte at that temperature. Its value is characteristic of every electrolyte, and characterizes its ability to dissociate. The higher the value of $K$, the more the electrolyte is dissociated.

## 9. Strengths of Acids and Bases

The strength of an acid or a base depends upon its degree of dissociation; higher the degree of dissociation, the greater the strength, and *vice versa*. For most weak acids and bases at moderate dillutions the degree of dissociation, $\alpha$, is very small, and so $(1-\alpha)$ in the equation $\frac{\alpha^2}{(1\times\alpha)V}=K$ may be taken as unity. The expression then becomes

$$\frac{\alpha^2}{V}=K \qquad \text{or,} \qquad \alpha^2=KV$$

so that

$$\alpha=\sqrt{KV}$$

Thus, the degree of dissociation, *i.e.*, the strength of a weak acid (or a weak base) is proportional to the square root of its dissociation constant. The dissociation constant, $K$ is generally preferred to the degree of dissociation as an index of the strength of an acid or a base because its value does not vary with concentration. Thus the relative strengths of weak acids and bases can be determined by comparing the values of their dissociation constants at the same temperature. In the case af acetic acid and hydrocyanic acid the dissociation constants at 25°C are as follows :

Acetic acid : $CHl_3.COOH \rightleftharpoons CH_3.COO^- + H^+$

$$\frac{[CH_3.COO^-][H^+]}{[CH_3.COOH]}=K_{CH_3.COOH}=1{\cdot}8\times10^{-5}$$

Hydrocyanic acid : $HCN \rightleftharpoons H^+ + CN^-$

$$\frac{[H^+][CN^-]}{[HCN]}=K_{HCN}=4{\cdot}1\times10^{-10}$$

This shows that acetic acid is a much stronger acid than hydrocyanic acid.

The dissociation constants of a few weak acids are given in Table 7-1. As the size of the constant increases, the degree of dissociation and, hence, the strength of the acid increases. Thus, HF is the strongest and HCN the weakest acid in the list.

**Table 7-1** *Dissociation constants of some weak acids*

| *Acid* | *Dissociation* | *K at 25°C* |
|---|---|---|
| 1. Hydrocynic acid | $HCN \rightleftharpoons H^+ + CN^-$ | $4{\cdot}1\times10^{-10}$ |
| 2. Hypochlorous acid | $HClO \rightleftharpoons H^+ + ClO^-$ | $5{\cdot}6\times10^{-8}$ |
| 3. Acetic acid | $CH_3.COOH \rightleftharpoons H^+ + CH_3.COO^-$ | $1{\cdot}8\times10^{-5}$ |
| 4. Formic acid | $H.COOH \rightleftharpoons H^+ + H.COO^-$ | $1{\cdot}8\times10^{-4}$ |
| 5. Nitrous acid | $HNO_2 \rightleftharpoons H^+ + NO_2^-$ | $4{\cdot}5\times10^{-4}$ |
| 6. Hydrofluoric acid | $HF \rightleftharpoons H^+ + ^-$ | $7{\cdot}2\times10^{-F4}$ |

**9-1. Strength of an acid and dilution.** The expression $\alpha = \sqrt{KV}$ derived above means that the degree of dissociation of a weak electrolyte is proportional to the square root of dilution. The data in Table 7-2 shows that the extent to which acetic acid, a weak electrolyte, dissociates increases with decreasing concentration, *i.e.*, with increasing dilution.

**Table 7-2** *Dissociation of acetic acid at different concentrations*

| *Molarity* | *% Dissociated* | $[H^+]$ *and* $[CH_3COO^-]$ | $[CH_3,COOH]$ | $K$ |
|---|---|---|---|---|
| 0·1 | 1·34 | 0·00134 | 0·09866 | $1{\cdot}82 \times 10^{-5}$ |
| 0·08 | 1·50 | 0·00120 | 0·07880 | $1{\cdot}83 \times 10^{-5}$ |
| 0·03 | 2·45 | 0·000735 | 0·02926 | $1{\cdot}85 \times 10^{-5}$ |
| 0·01 | 4·15 | 0·000415 | 0·009585 | $1{\cdot}80 \times 10^{-5}$ |

## 10. Ionic Product of Water

Though a very poor conductor of electricity, pure water still has a very slight but measurable conductivity. This is because water does dissociate, though extremely slightly, according to the equation

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^{-*}$$

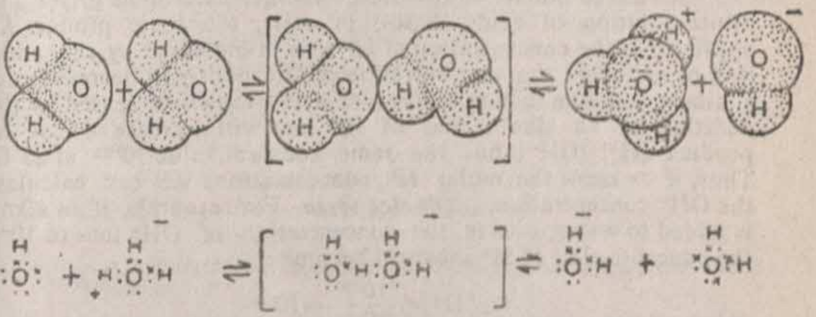

Fig. 7-4. Self dissociation of water.

Or, more simply :

$$H_2O \rightleftharpoons H^+ + OH^-$$

---

*The self-dissociation of water is analogous to the ionization of hydrogen chloride in water, and involves the rupture of the H—O bond in one water molecule by interaction with another water molecule.

Ionization of HCl : $H_2O + H \vdots Cl \rightleftharpoons H_3O^+ + Cl^-$

Ionization of $H_2O$ : $H_2O + H \vdots O{-}H \rightleftharpoons H_3O^+ \; OH^-$

Applying the law of mass action to the ionization of water

$$\frac{[H^+][OH^-]}{[H_2O]}=K$$

$$\therefore \quad [H^+][OH^-]=K[H_2O]$$

However, the dissociation of water into ions occurs to such a small extent that even if it is increased a thousandfold, there will be negligible precentage change in the value of $[H_2O]$. Therefore, the concentration of undissociated water, $[H_2O]$, may be regarded as constant

$$\therefore \quad [H^+][OH^-]=K\times\text{constant}=K_w$$

The constant $K_w$ is known as the *ionic product for water*.

Since water dissociates to give the same number of hydrogen and hydroxyl ions, the concentration of these two ions must necessarily be the same in pure water. Electrical conductivity measurements show that this concentration is $10^{-7}$ gram ions per litre at 25°C. Therefore, the value of $K_w$ at 25°C is $10^{-7}\times10^{-7}$ or $1\times10^{-14}$. The value of $K_w$ increases rapidly with temperature and at 100°C is approximately $5\times10^{-13}$, about 50 times as large as at 25°C. This means that the degree of dissociation of water and the concentration of $H^+$ and $OH^-$ ions increase with rising temperature.

Wherever water is involved, whether pure or as solvent, in dilute solution of acids, bases, or salts, the ionic product $K_w$ applies. If the concentration of $H^+$ ions in increased by the addition of an acid, the concentration of $OH^-$ ions will decrease and, similarly, if the concentration of $OH^-$ ions is increased by the addition of an alkali, that of $H^+$ ions will decrease so that the product $[H^+][OH^-]$ has the same constant value $10^{-14}$ at 25°C. Thus, if we know the molar $H^+$ concentration, we can calculate the $OH^-$ concentration, and *vice versa*. For example, if an alkali is added to water, raising the concentration of $OH^-$ ions to $10^{-5}$. the concentration of $H^+$ ions will become :

$$[H^+]=\frac{10^{-14}}{10^{-5}}=10^{-9}$$

It is also clear from this that in any solution in which water is a solvent, both $H^+$ and $OH^-$ ions are present, even in concentrated acid or concentrated alkali solutions. *Solutions* in which the concentration of hydrogen and hydroxyl-ions is the same and equals $10^{-7}$ gram-ions per litre are called neutral solutions. In acid solutions the concentration of hydrogen-ion is higher; in alkaline solutions the concentration of hydroxyl-ion is higher.

## 11. The pH

The concentration of the hydrogen ion is not only a measure of acidity of a solution but also of its basicity, since the hydroxyl ion concentration can be deduced from the relationship $[OH^-] = \frac{10^{-14}}{[H^+]}$ at 25°C. Instead of expressing the hydrogen ion concentration by actual values, it is more convenient to express it in terms of the negative logarithm of the concentration. The negative logarithm of the hydrogen ion concentration is called the pH of the solution. Expressed mathematically,

$$pH = -\log [H^+]$$

or,
$$pH = \log \frac{1}{[H^+]}$$

In words, the pH is the logarithm to the base 10 of the ***reciprocal*** of the hydrogen ion concentration, $[H^+]$. The object of using the reciprocal of the $H^+$ ion concentration is to obtain a scale on which all the values normally encountered are positive.

**Example 1.** *Find the pH of a solution whose hydrogen ion concentration is $2 \times 10^{-6}$ M*

$$\begin{aligned} pH &= -\log [H^+] \\ &= -\log [2 \times 10^{-6}] \\ &= -(\log 2 + \log 10^{-6}) \\ &= -(0{\cdot}3 + 6) \text{ from the table of logarithm to the base 10} \\ &= -(-5{\cdot}7) \\ &= 5{\cdot}7. \end{aligned}$$

**Example 2.** *Calculate the hydrogen ion concentration of a solution whose pH is 4·25.*

$$pH = -\log [H^+] = 4{\cdot}25$$

or,
$$\log [(H^+] = -4{\cdot}25$$

Since logarithm tables contain only positive mantissas, we must work $-4{\cdot}25$ as $-5 + 0{\cdot}75$. Then

$$\begin{aligned} \log [H^+] &= 0{\cdot}75 - 5 \\ [H^+] &= \text{antilog of } (0{\cdot}75 - 5) \\ [H^+] &= (\text{antilog of } 0{\cdot}75) \times (\text{antilog of } -5) \\ [H^+] &= 5{\cdot}6 \times 10^{-5} \end{aligned}$$

That is, the hydrogen ion concentration corresponding to the pH of 4·25 is $5{\cdot}6 \times 10^{-5}$ moles per litre.

In neutral solutions $[H^+] = 10^{-7}$ and therefore, pH = 7. Acidic solutions have a higher concentration of $H^+$ ions and, therefore, their pH values are less than 7; the more acidic the solution, the smaller is its pH. In alkaline solutions, pH is more than 7 and the higher the alkalinity, the larger it is. It must be noted that the pH scale being logarithmic, a change of only one unit corresponds to a tenfold change in the hydrogen ion concentration.

## 12. Indicators

Certain organic substances exhibit a change of colour in dilute solution when the pH of the solution changes. For example phenolphthalein is colourless in aqueous solutions having pH less than 9, but shows pink colour in solutions having a higher pH.

Similarly, methyl orange shows red colour in aqueous solutions having pH up to 3·1 and yellow colour in solutions having pH higher than 4·4. Substances like phenolphthalein are called *acid-base indicators* or **pH indicators.**

pH indicators are either weak organic acids or weak organic bases which dissociate to give an ion of a colour different from the colour of the undissociated form. For example, methyl orange is red in the undissociated form but dissociates to give an anion which is yellow. If methyl orange, a weak acid, is shown by the formula HIn, its dissociation may be represented by the equation

$$\underset{\text{red}}{HIn} \rightleftharpoons H^+ + \underset{\text{yellow}}{In^-}$$

In a strongly acidic solution (high concentration of $H^+$), the equilibrium will be shifted towards the undissociated form, HIn, in accordance with the law of mass action, and red colour would predominate. In a solution with a low concentration of $H^+$ ions the equilibrium shifts to the right so that the yellow colour of the anion $In^-$ is observed. In any given solution, the colour exhibited by the indicator is determined by the ratio of the concentrations of the undissociated form and the coloured ion. When the pH of the solution is 3·1, about 90 per cent of the indicator is present in the red form and 10 per cent is present in the yellow form. The colour of the solution is seen red. With further increase in the pH, the concentration of the red form will increase. However, no colour change will be observed since the eye cannot detcet any colour change if the ratio of the concentration of the two types of coloured particles is more than 10 : 1.

At a pH of 4·4 about 90 per cent of methyl orange is in the form of the yellow ion, and the colour of the solution is yellow. Further increase in pH does not change the colour despite an increase in the concentration of the yellow form for the reason mentioned above. The pH range 3·1 to 4·4 is called the colour-change interval of the indicator. It is between these two pH values that any pronounced colour change takes place.

A large number of acid-base indicators are known which change colour over widely different ranges of pH values (Table 15·3). By using a number of indicators, and by a process of elimination, the pH of a solution can be fixed within rather narrow limits.

**Table 7-3** *Some acid-base Indicators*

| *Indicator* | *Colour in the more acid range* | *pH pange* | *Colour in the more basic range* |
|---|---|---|---|
| Thymol blue | pink | 1·2—2·8 | yellow |
| Methyl orange | pink | 3·1—4·4 | yellow |
| Methyl red | red | 4·4—6·3 | yellow |
| Litmus | red | 4·7—8·2 | blue |
| Phenolphthalein | colourless | 8·3—10·0 | pink |
| Thymolphthalein | colourless | 9·3—10·5 | blue |
| Alizarin yellow | colourless | 10·1—12·1 | yellow |

The measurement and control of pH are important in scientific investigations, in industry, and in agriculture. The separation and identification of many of the metallic ions depend on the pH of the solutions in which they are present.

**12-1. The choice of a pH indicator in titration.** The suitable pH indicators for various types of titrations (neutralization reactions) are shown in Table 7-4.

**Table 7-4** *Suitable neutralisation indicators*

| *Type of titration* | *Suitable indicator* |
|---|---|
| 1. Strong acid—strong base | Any indicator |
| 2. Weak acid—strong base | Phenolphthalein |
| 3. Strong acid—weak base | Methyl orange or methyl red |
| 4. Weak acid—weak base | No indicator is satisfactory |

## 13. Hydrolysis of Salts

An aqueous solution of a salt of a strong acid and a strong base, *e.g.*, sodium chloride, has a pH of about 7 and is therefore neutral. However, salts of strong acids and weak bases, *e.g.*, ammonium chloride, give acidic solutions when dissolved in water while the salts of weak acids and strong bases, *e.g.*, sodium acetate, give alkaline solutions. Obviously, the ions of these types of salts react with water in such a way that either the $H^+$ ions or the $OH^-$ ions formed by the self-dissociation of water are removed, causing the other ion to be in excess.

*The interaction of a salt with water accompanied by a change in the concentration of the ions of water is called hydrolysis of that salt.*

Consider a salt MA made from the base MOH and the acid HA dissociating in aqueous solution according to the equation

$$MA \rightleftharpoons M^+ + A^- \qquad ...(1)$$

($M^+$ stands for the metal ion, and $A^-$ for the anion)
The solvent water also dissociates to a very small extent :

$$H_2O \rightleftharpoons H^+ + OH^- \qquad ...(2)$$

These four types of ions in solution give rise to two further equilibria :

$$M^+ + OH^- \rightleftharpoons MOH \qquad ...(3)$$

and,

$$H^+ + A^- \rightleftharpoons HA \qquad ...(4)$$

Whether the resulting solution will be acidic or alkaline will depend on the *relative* strengths of the base MOH and the acid HA from which the salt MA is derived. Thus, in discussing the phenomenon of hydrolysis, four types of salts need consideration.

*Type 1. Salts of weak acids and strong bases.* The hydrolysis of this type of salts may be illustrated by the example of sodium acetate, $CH_3.COONa$. It is the salt of the strong base NaOH and the weak acid $CH_3.COOH$ (acetic acid). When dissolved in water, sodium acetate dissociates completely into $Na^+$ and $CH_3.COO^-$ ions.

$$\underset{\text{sodium acetate}}{CH_3.COONa} \rightleftharpoons \underset{\text{sodium ion}}{Na^+} + \underset{\text{acetate ion}}{CH_3.COO^-}$$

In addition, the solution also contains small amounts of $H^+$ and $OH^-$ ions from the feeble dissociation of water. Since sodium hydroxide is a strong base and completely dissociates into $Na^+$ and $OH^-$ ions, the final condition with regard to these two ions remains unchanged. On the other hand, acetic acid is a very weak acid and, therefore, $CH_3.COO^-$ ions combine with the $H^+$ ions to form undissociated $CH_3.COOH$ molecules. The removal of $H^+$ ions in this manner causes the equilibrium between the molecules of water and its ions

$$H_2O \rightleftharpoons H^+ + OH^-$$

to shift to the right so that more $H^+$ and $OH^-$ ions are formed. The net result is that there is a certain excess of $OH^-$ ions in solution which, therefore, reacts alkaline. The net reaction may be expressed by the ionic equation

$$CH_3.COO^- + H_2O \rightleftharpoons CH_3.COOH + OH^-$$

or in the molecular form,

$$CH_3.COONa + H_2O \rightleftharpoons CH_3.COOH + NaOH$$

Salts of weak acids and strong bases, then, hydrolyse by the interaction of their anions which water as a result of which the parent acid and base are produced. The extent of hydrolysis depends on the relative strength (or weakness) of the parent acid. The weaker the acid, the greater the hydrolysis because of the greater tendency to form the undissociated molecules of the acid.

Other examples of this type of salts are sodium carbonate ($Na_2CO_3$), potassium cyanide (KCN), sodium hypochlorite (NaClO), etc. The reactions of the anions of these salts with water can be represented by the following ionic equations :

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$
$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$
$$ClO^- + H_2O \rightleftharpoons HClO + OH^-\text{, respectively.}$$

*Type 2. Salts of strong acids and weak bases.* In this type of salts the conditions are just reverse of those for type 1. Here the cations of the salts combine with the hydroxyl ions of water, while the anions remain free. Consider the hydrolysis of ammonium chloride, $NH_4Cl$, a salt of a weak base $NH_4OH$ and a strong acid HCl. When dissolved in water, it dissociates into $NH_4^+$ ions and $Cl^-$ ions. The $NH_4^+$ ions combine with the $OH^-$ ions of water to produce undissociated $NH_4OH$. There is, however, no permanent link up between the $H^+$ and $Cl^-$ ions since the corresponding acid, HCl, is 100 per cent ionised in solution. The removal of $OH^-$ ions from the solution by the $NH_4^+$ ions causes the equilibrium

$$H_2O \rightleftharpoons H^+ + OH^-$$

to shift to the right. As a result, an excess of $H^+$ ions is left in the solution which, therefore, becomes acidic. The reaction that takes place is represented by the ionic equation

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

or, in the molecular form

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl.$$

In the case of such salts, the weaker the parent base, the greater will be the extent of hydrolysis because of the weaker tendency of the base to dissociate.

Two more examples of salts of this type are copper (II) chloride and iron (III) chloride. The hydrolysis of copper (II) chloride is represented by the ionic equation

$$Cu^{2+} + H_2O \rightleftharpoons Cu(OH)^+ + H^-$$

or, in the molecular form

$$CuCl_2 + H_2O \rightleftharpoons Cu(OH)Cl + HCl.$$

In the case of iron (III) chloride, the hydrolysis may be expressed as

$$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$$

or,

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$$

*Type 3. Salts of weak acids and weak bases.* Both the anion and cation of the salt of this type react with the water to produce $OH^-$ and $H^+$ ions respectively. Strong hydrolysis therefore occurs in water solution. Whether the solution of such a salt will be acidic or basic will depend upon the relative strengths of the parent base and the parent acid formed. Should the parent base be comparatively stronger than the parent acid, the solution will be basic, and *vice versa.* Should the two be equally strong, the solution will be neutral. Thus, the solution of calcium acetate, $(CH_3.COO)_2Ca$, is slightly basic, that of ammonium formate, $H.COONH_4$, is slightly acidic, and that of ammonium acetate, $CH_3.COONH_4$, is very nearly neutral. The hydrolysis of ammonium acetate may be represented by the equation

$$NH_4^+ + CH_3.COO^- + H_2O \rightleftharpoons NH_4OH + CH_3.COOH.$$

Salts of this type are difficult to keep even in air as they react with the atmospheric moisture, and hydrolyse. This is why odours of both ammonia (by the decomposition of $NH_4OH$) and acetic acid are perceived when ammonium acetate is exposed to air.

*Type 4. Salts of strong acids and strong bases.* Salts of this type, *e.g.*, sodium chloride, sodium sulphate, potassium nitrate, etc., do not undergo hydrolysis, and form neutral solutions in water. This is because the ions of such salts do not react with water. Thus in the case of sodium chloride neither the $Na^+$ ions combine with the $OH^-$ ions of the water nor do the $Cl^-$ ions combine with the $H^+$ ions. Therefore, the concentrations of both hydrogen ion and hydroxyl ion in solution remain the same as in pure water, and the solution behaves neutral.

## 14. Common-Ion Effect

Consider the dissociation of ammonium hydroxide, a weak base :

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

The equilibrium constant of this dissociation reaction

$$K_{NH_4OH} = \frac{[NH_4^+]\,[OH^-]}{[NH_4OH]}$$

has a constant value at any given temperature.

Suppose some ammonium chloride is added to the ammonium hydroxide solution. Since ammonium chloride is completely dissociated in solution, a very small quantity of this salt will cause enormous increase in the $NH_4^+$ ion concentration. This affects the equilibrium between the undissociated $NH_4OH$ molecules and its component ions. As a consequence $NH_4^+$ and $OH^-$ ions combine to form undissociated $NH_4OH$ until the expression $\frac{[NH_4^+]\,[OH^-]}{[NH_4OH]}$ is again equal to $K_{NH_4OH}$ at that temperature. That is, the concentration of $OH^-$ ions in solution and the extent of dissociation of ammonium hydroxide is decreased. Thus, adding ammonium chloride, which has the $NH_4^+$ ion common with ammonium hydroxide, reduces the basicity (*i.e.*, the $OH^-$ ion concentration) of the solution without changing the total quantity of the base.

*The decrease in the degree of dissociation of a weak electrolyte caused by the introduction of an ion in common with the electrolyte is said to be the result of the* **common ion effect.**

Similarly, the dissociation of hydrogen sulphide—a weak acid, is suppressed in the presence of hydrochloric acid. The latter being a very strong acid completely dissociates to give a high concentration of $H^+$ ion, causing the equilibrium

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

to shift to the left. The concentration of the free $S^{2-}$ ions in solution is thus greatly lowered.

It may be noted that the results of common-ion effect can be correctly predicted and explained by applying the Le Chatelier's principle to the ionic equilibria under consideration.

**14·1. Some applications of common-ion effect*** (1) The suppression of the dissociation of hydrogen sulphide (or, hydrosulphuric acid) by using hydrochloric acid and of ammonium hydroxide by using ammonium chloride forms the basis of separating the sulphides and hydroxides of the metals in various groups in the systematic scheme of qualitative analysis.

(2) In the gravimetric estimation of silver by precipitating $Ag^+$ ions as AgCl, excess of $Cl^-$ ions is added to ensure maximum precipitation of AgCl. The extra $Cl^-$ ions shift the equilibrium in a saturated solution of AgCl

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

to the left, so that most of the $Ag^+$ ions are precipitated as AgCl.

## 15. Buffer Solutions

Good use is made of the common-ion effect in the preparation of *buffer solutions*. These are *solutions which resist changes in pH upon dilution or upon addition of small amounts of either strong acid or strong base* Commonly used buffer solutions are mixtures of either weak acids and their salts with strong bases, *e.g.*, acetic acid and sodium acetate, or of weak bases and their salts with strong acids, *e.g.*, ammonium hydroxide and ammonium chloride.

To understand how a buffer solution works consider a solution containing acetic acid and sodium acetate. Since acetic acid dissociates only feebly** and sodium acetate is completely dissociated, the solution will have relatively large amounts of sodium ions, acetate ions, and undissociated acetic acid molecules, and only a small amount of $H^+$ ions.

$$\underset{\text{Relative concn.}}{}\quad CH_3.COONa \rightarrow \underset{\text{high}}{Na^+} + \underset{\text{high}}{CH_3.COO^-}\ (\textit{100\% dissociation})$$

$$\underset{\text{Relative concn.}}{}\quad \underset{\text{high}}{CH_3.COOH} \rightleftharpoons \underset{\text{low}}{H^+} + \underset{\text{low}}{CH_3.COO^-}\ (\textit{slight dissociation}).$$

When a strong acid such as HCl is added to this buffer, the added $H^+$ ions combine with the large reserve of $CH_3.COO^-$ ions present causing the second equilibrium to shift to the left. This effectively reduces the $H^+$ ion concentration again. On the other hand, when a strong base such as NaOH is added, the $H^+$ ions from the acid combine with the $OH^-$ ions introduced to form undissociated molecules of water. The second equilibrium thereby shifts to the right and more $H^+$ ions are produced by the dissociation of acetic acid. Thus, in both cases the low concentration of $H^+$ ions, *i.e.*, the pH of the solution, remains nearly the same. As long as appreciable amounts of $CH_3.COO^-$ and $CH_3.COOH$ are present, the system will serve as a buffer.

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*The precipitation of pure sodium chloride by passing hydrogen chloride through a saturated solution of the former is often quoted as an example of the common-ion effect (the common ion being $Cl^-$). However, the common-ion effect is not the only reason since sodium chloride is also precipitated by passing hydrogen bromide through the solution The more important reason is that a considerable quantity of water molecules is used up in solvating the ion produced when these highly soluble gases dissolve in water so that the effective concentration of sodium chloride in the solution is increased.

**The dissociation of acetic acid is all the more feeble in the presence of sodium acetate due to the common-ion effect.

The chief use of buffer solutions in the laboratory is for making solutions of known and constant pH values. The pH values of such solutions do not change by the dissolution of atmospheric carbon dioxide (an acidic gas) or of alkali from the glass vessel. By a suitable choice of substances it is possible to prepare buffer solutions of any desired pH between 1 and 13. Some buffer pairs that find extensive applications are phthalic acid—potassium hydrogen phthalate, acetic acid—sodium acetate, boric acid—borax (sodium tetraborate), and sodium hydroxide—borax. Human blood contains a highly effective buffer mixture of carbonic acid (dissolved carbon dioxide) and its salt sodium hydrogen carbonate ($NaHCO_3$). When excess $H^+$ ion enters the blood stream it is removed by the reaction

$$H^+ + HCO_3^- \rightarrow H_2CO_3$$

and when excess alkali is formed, it is eliminated by the reaction.

$$OH^- + H_2CO_3 \rightarrow H_2O + HCO_3^-$$

The pH of the blood thus remains very nearly 7·35 (slightly alkaline), and a change of ±0·5 would probably be fatal. Buffer solutions are widely used in processed foods and drinks so that they would not cause excessive acidity.

## 16. Solubility Product

Every ionic compound, howsoever insoluble in water it may seem to be, still dissolves in it to some measureable extent If the compound is in contact with water long enough, a saturated solution of its ions is formed which is in equilibrium with the undissolved solid. At equilibrium the solid continues to dissolve at the same rate at which the opposite process of recrystallization is taking place. This can be represented by a reversible equation. For example, in a saturated solution of silver chloride in equilibrium with some solid silver chloride :

$$AgCl\ (\textit{solid}) \underset{\text{recrystallization}}{\overset{\text{dissolution}}{\rightleftharpoons}} Ag^+ + Cl^-\ (\textit{in saturated solution})$$

Applying the law of mass action to this system, we get

$$\frac{[Ag^+]\,[Cl^-]}{[AgCl]} = K_c$$

Or, $$[Ag^+]\,[Cl^-] = K_c \times [AgCl].$$

Because the concentration of the solid silver chloride is constant at constant temperature, the two constants may be lumped together to obtain a new constant. That is,

$$[Ag^+]\,[Cl^-] = K_c \times \text{constant} = K_{sp}$$

The new constant $K_{sp}$ is called the solubility product since its value characterizes the ability of the compound to dissolve. It may be defined as follows :

*The product of the concentrations of the ions of a slightly soluble electrolyte in its saturated solution is constant at a given temperature, and is called the solubility product of that electrolyte.*

If the slightly soluble electrolyte contains more than one ion of one kind in its formula, the concentration of that ion is raised to the corresponding power in its solubility product expression. For example, in the case of $Mg(OH)_2$,

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-; \; K_{sp} = [Mg^{2+}]\,[OH^-]^2$$

and in the case of calcium phosphate, $Ca_3(PO_4)_2$,

$$Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}; \; K_{sp} = [Ca^{2+}]^3\,[PO_4^{3-}]^2.$$

The solubility product principle is valid only for slightly soluble electrolytes and does not hold for moderately soluble salts such as sodium chloride, silver nitrate, etc. The ion concentrations in the saturated solutions of such compounds are always very small, and when squared or cubed yield still smaller numbers. Therefore, the numerical value of solubility product is always very small, rarely exceeding $10^{-2}$ and being as low as $1{\cdot}6 \times 10^{-72}$ for $Bi_2S_3$.

**16-1. Applications of solubility product.** The solubility product indicates the maximum value of the ionic product in the solution of a slightly soluble electrolyte. Two conclusions may be drawn from this :

(*i*) When the product of the ion concentrations exceeds the solubility product for a given compound in a solution, some of it is precipitated so that the ion concentrations decrease. Precipitation occurs until the product of the ionic concentrations falls to the value of the solubility product of the compound. Hence, in order to precipitate a slightly soluble electrolyte, its ions must be brought together in the same solution in such quantities that the product of the ion concentrations, raised to the appropriate powers, exceeds the solubility product of the compound.

(*ii*) When the product of the ion concentrations is less than the solubility product, the solution is unsaturated and the substance will remain in solution.

The applications of solubility product to qualitative and quantitative analysis, described below, are based on the above conclusions.

**1. Division of cations in groups.** The division of cations in six groups in the qualitative analysis is based on the consideration of solubility products of their slightly soluble salts. For example, when HCl is added to a solution containing various metal cations, the solubility products of only AgCl, $Hg_2Cl_2$, and $PbCl_2$ are exceeded which are precipitated. Hence, the cations $Ag^+$, $Hg_2^{2+}$

and $Pb^{2+}$ are placed in a separate group, *viz.*, group I. In the same way, other cations have been placed in other groups.

**2. Precipitation of sulphides.** If $H_2S$ is passed through a solution containing cations other than those of group I, the solubility products of all metal sulphides (which do not undergo hydrolysis) are exceeded, and all of them are precipitated. If some HCl is added to the solution before passing $H_2S$, the $S^{2-}$ ion concentration is greatly decreased due to the common-ion effect. At the decreased concentration of the $S^{2-}$ ion, the ionic product of metal sulphides, $[M^{2+}]\ [S^{2-}]$, becomes less than the solubility products of FeS, MnS, ZnS, NiS, and CoS. These sulphides are, therefore, not precipitated. The sulphides of $Pb^{2+}$, $Hg^{2+}$, $Bi^{3+}$, $Cu^{2+}$, $Cd^{2+}$, $Sn^{2+}$, $As^{3+}$, and $Sb^{3+}$ are precipitated as their solubility products are still exceeded by the product of ionic concentrations. These cations constitute group II of the qualitative analysis.

The cations $Mn^{2+}$, $Zn^{2+}$, $Ni^{2+}$, and $Co^{2+}$ are precipitated as their sulphides in group IV when $H_2S$ is passed through ammoniacal solution. The $S^{2-}$ ion concentration from $H_2S$ under this conditions is high enough for the product of ionic concentrations to exceed the solubility products of these metal sulphides. These cations constitute group IV of the qualitative analysis.

The description given above will be clear from the values of the solubility products of some metal sulphides given in Table 7-5.

**Table 7-5** *Soiubility products of some metal Sulphides at 25°C*

| *Metal Sulphide* | *Solubility product* | *Metal Sulphide* | *Solubility product* |
|---|---|---|---|
| 1. HgS | $3{\cdot}2 \times 10^{-53}$ | 7. FeS | $1{\cdot}0 \times 10^{-19}$ |
| 2. $Bi_2S_3$ | $1{\cdot}6 \times 10^{-72}$ | 8. MnS | $5{\cdot}6 \times 12^{-16}$ |
| 3. PbS | $1{\cdot}0 \times 10^{-29}$. | 9. ZnS | $1{\cdot}2 \times 10^{-23}$ |
| 4. CuS | $2{\cdot}5 \times 10^{-50}$ | 10. NiS | $3{\cdot}0 \times 10^{-21}$ |
| 5. CdS | $3{\cdot}6 \times 10^{-29}$ | 11. CoS | $7{\cdot}0 \times 10^{-23}$ |
| 6. SnS | $8{\cdot}0 \times 10^{-29}$ | | |

**3. Precipitation of hydroxides.** The cations $Fe^{3+}$, $Al^{3+}$, and $Cr^{3+}$ are precipitated as their hydroxides in group III by adding $NH_4OH$ to the solution to which $NH_4Cl$ has been added. In the presence of $NH_4Cl$, the $OH^-$ concentration from $NH_4OH$ is greatly reduced due to the common-ion effect. At the reduced concentration of the $OH^-$ion, only the metal hydroxides of very low solubility products, *viz.*, $Fe(OH)_3$, $Al(OH)_3$, and $Cr(OH)_3$) are precipitated The hydroxides of group IV cations ($Zn^{2+}$, $Mn^{2+}$, $Ni^{2+}$, $Co^{2+}$) and $Mg^{2+}$ are not precipitated as their solubility products are very high.

**4. Precipitation for gravimetric estimations.** In gravimetric estimations, an excess of the precipitating agent is always added to the solution to ensure complete precipitation. For example, if in the precipitation of barium sulphate by the addition of sulphuric acid ($Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4 \downarrow$), the latter is added in equivalent amount, a small quantity of $BaSO_4$ will be left behind in solution. If sulphuric acid is added in excess, the product of ionic concentrations, $[Ba^{+2}]\ [SO_4^{2-}]$ far exceeds the solubility product of $BaSO_4$, causing a more complete precipitation.

5. **Fractional precipitation.** When two cations form sparingly soluble compounds with the same anion, or when two anions form sparingly soluble compounds with the same cation, the compound with a lower value of solubility product will precipitate first on the addition of the precipitant to a sultion containing both. Consider a solution containing both $Cl^-$ and $I^-$ ions. When silver nitrate is added, silver iodide ($K_{sp} = 1{\cdot}5 \times 10^{-16}$) is precipitated first, and only after most of the iodide is precipitated does silver chloride ($K_{sp} = 1{\cdot}2 \times 10^{-10}$) begin to precipitate.

## Questions

### I. Ionic Theory

1. List four differences in behaviour between solutions of electrolytes and non-electrolytes.

2. Account for the electrical neutrality of the solutions ef electrolytes.

3. What are the main points of Arrhenius' Ionic Theory ?

4. Show, by means of equations, the dissociation of phosphoric acid ($H_3PO_4$) in aqueous solutions.

5. How does a hydronium ion differ from a hydrogen ion ? How is the hydronium ion produced ?

6. Solutions of electrolytes exert higher osmotic pressure and show larger depression of freezing point or elevation of boiling point than solutions of non-electrolytes of the same molality. Explain the apparently anomalous behaviour of electrolytes in solution.

7. How does the electrical conductivity of the solutions of electrolytes provide an evidence in favour of the ionic theory ?

8. Explain the reason why the reactions occuring between electrolytes in water solutions are very fast while those involving non-electrolytes are usually slow.

9. Why are the ions generally less reactive than the atoms from which they are formed ?

10. Distinguish between electrolytic dissociation and ionization with the aid of suitable examples.

11. Dry liquid hydrogen chloride is a non-conductor of electricity whereas the same substance in aqueous solution is a conductor. Explain.

12. What factors affect the degree of dissociation of electrolytes, and how ?

13. Account for the fact that if sodium chloride is completely dissociated in aqueous solution, why does a molal solution of NaCl in water does not cause exactly twice the rise in boiling point or twice the lowering of freezing point of a molal sugar solution.

14. Explain with the aid of suitable examples the meaning of term *activity coefficient*.

15. Explain the following facts :

(*a*) A 1M solution of $CH_3.COOH$ (acetic acid) conducts the current much more feebly than does a 1M solution of HCl.

(*b*) A 1M solution of $MgCl_2$ has a lower freezing point than a 1M solution of NaCl.

(*c*) A 1M solution of KBr has the same freezing point as a 1M solution of NaCl.

(*d*) 1M solutions of ethyl alcohol and glycerol have the same freezing point.

16. Which will be a better conductor of electricity concentrated $H_2SO_4$ or dilute $H_2SO_4$, and why ?

17. How does the ionic theory explain why all acid or all basic solutions, regardless of formula, affect indicators in the same way ?

18. How do you explain the fact that zinc will readily liberate hydrogen from cold, dilute $H_2SO_4$ but not from cold, conc. $H_2SO_4$.

19. Account for the fact that silver nitrate solution gives a precipitate of silver chloride with sodium chloride but not with ethyl chloride.

20. Why is it that the apparent degree of dissociation of a strong electrolyte approaches 100 per cent as the solution is made more dilute ?

21. Why do not the crystalline ionic compounds conduct electricity although they are 100 per cent ionized ?

**II. Ionic Equilibria**

22. Give the mathematical form of Ostwald's Dilution Law and state what the various symbols in it stand for. What is the significance of the *dissociation constant* ?

23. Explain by applying Ostwald's Dilution Law why the strength of a weak acid or a weak base increases with dilution.

24. Why does the law of chemical equilibrium apply to solutions of weak electrolytes but not to solutions of strong electrolytes ?

25. Show by means of electron-dot formulae the self-dissociation of water ? Give the expression for the ionic product of water and state its value at 25°C.

26. How is the ionic product of water affected when an acid or a base is dissolved in water ? Explain your answer.

27. What is the concentration of $H^+$ ion in pure water ? Of $OH^-$ ion ?

28. Define the *p*H. What is the *p*H of a neutral solution ? What is th value of the *p*H in an acid solution ? In a basic solution ?

29. Discuss the action of acid-base indicators with particular reference to methyl orange.

30. Name your choice of a *p*H indicator in titration involving

(*a*) strong acid—strong base,
(*b*) weak acid—strong base,
(*c*) strong acid—weak base,
(*d*) weak acid—weak base.

31. Define hydrolysis. Explain the hydrolysis of the various types of salts by means of chemical equations only.

32. What types of salts do not hydrolyze and why ?

33. Without removing any solute (*a*) what could you add to reduce the $NH_4^+$ ion concentration in a solutions of $NH_4OH$ ? (*b*) What would you add to reduce the $OH^-$ ion concentration ? (*n*) What name is associated with this process ?

34. How does the *p*H of a solution containing both acetic acid and sodium acetate compare with that of a solution containing the same concentration of acetic acid alone ? Explain your answer.

35. State two applications of the common-ion effect in qualitative analysis.

36. What constitutes a buffer solution ? How does a buffer solution resist changes in *p*H upon addition of small amounts of either strong acid or strong base ?

37. Of what practical value are buffer solutions ?

38. Which way would the *p*H shift when each of the following is added to the pure water :

$CaO$, $KCl$, $NH_4Cl$; $CuSO_4$, $CO_2$, sodium acetate ?

39. Explain why a 1M acetic acid solution has a higher *p*H than a 1M hydrochloric acid solution.

40. A saturated solution of a slightly soluble electrolyte in contact with some solid electrolyte is a system in equilibrium. Explain.

41. Define 'solubility product'. Write the expression for the solubility product of each of the following slightly soluble electrolytes :

$AgBr$, $Ba_3(PO_4)_2$, $Ag_2S$, and $PbCl_2$.

## Key

1. (*i*) Solutions of electrolytes conduct electric current, of non-electrolytes do not.

(*ii*) Solution of electrolytes exert higher osmotic pressure than the solution of non-electrolytes of same molality.

(*iii*) Solutions of electrolytes show larger elevation of boiling points than the solutions of non electrolytes of same molality.

(*iv*) Solutions of electrolytes show larger elevation of boiling point than the solutions of non-electrolytes of same molality.

2. The electrical neutrality of the solutions of electrolytes is due to the fact that the total negative charge on the anions is equal to the total positive charge on the cations in solution.

6. Osmotic pressure, freezing point lowering, and boiling point rise are all colligative properties, *i.e.*, dependent on the number of particles of solute in the solution. Since the molecules of electrolytes dissociate into ions, each ion having the same colligative effect as an undissociated molecule, electrolytes exert higher osmotic pressure and show larger depression of freezing point and larger elevation of boiling point than the solutions of non-electrolytes of same molality.

8. Electrolytes in water solutions are already separated into ions in water solutions. These ions are the reacting species and can quickly unite with oppositely charged ions because of their mutual electrostatic attraction. In

the case of covalent molecules, energy is first required to break or *activate* the molecules, so that they may react with each other. This often takes time and considerable heat energy.

9. The electronic structure of any ion is more stable than that of the atom from which it is formed by transfer of electrons For example, both $Na^+$ and $Cl^-$ ions have stable outer shells of 8 electrons whereas the corresponding atoms Na and Cl have unstable electron shells of 1 and 7 electrons respectively.

$$Na : 2,8,1 ; \quad Na^+ : 2,8$$
$$Cl : 2,8,7 ; \quad Cl^- : 2,8,8$$

11. Dry hydrogen chloride is a covalent compound, $H \times \underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$ , and does not contain ions. Hence, it does not conduct electricity. In aqueous solution, it reacts with water to give hydronium and chloride ions, so that the aqueous solution conducts electricity.

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

13. Sodium chloride dissociates in solution as

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

However, the attraction between the oppositely charged $Na^+$ and $Cl^-$ ions prevents them from acting as independent, individual particles. Hence, the apparent number of ions is smaller than their actual number.

15. (*a*) Acetic acid is a weaker acid than hydrochloric acid, *i.e.*, ionizes in solution to a less degree.Hence, 1M solution of $CH_3.COOH$ has much smaller number of ions than 1M solution of HCl and, therefore, conducts the current much more feebly than the latter.

(*b*) $MgCl_2$ dissociates as $MgCl_2 \rightleftharpoons Mg^{2+} + 2Cl^-$ ; NaCl dissociates as $NaCl \rightleftharpoons Na^+ + Cl^-$. That is, each 'molecule' of $MgCl_2$ gives 3 ions whereas each 'molecule' of NaCl gives only 2 ions. Hence, 1M solution of $MgCl_2$ has larger number of ions than a 1M solution of NaCl and, therefore, has a lower freezing point.

(*c*) 1M solutions of both KBr and NaCl will have the same number of ions ($KBr \rightleftharpoons K^+ + Br^-$ ; $NaCl \rightleftharpoons Na^+ + Cl^-$).

(*d*) Both alcohol and glycerol are non-electrolytes and do not dissociate in solutions. Hence, 1M solutions of both have the same number of molecules and therefore, the same freezing point.

16. Dilute $H_2SO_4$ will be a better conductor since the degree of dissociation, *i.e* , the number of ions, will increase with dilution.

17. All acids and bases furnish the same common ion, $H^+$ and $OH^-$ respectively, to the solution. It is the $H^+$ ion in the case of acids and the $OH^-$ ion in the case of bases which affects the colour of the indicator rather than the entire acid or base.

18. Concentrated sulphuric acid is a covalent compound and does not contain $H^+$ ions. When diluted with water, it reacts with water molecules to give hydrogen ions and sulphate ions.

$$H_2SO_4 + 2H_2O \rightarrow 2H_3O^+ + SO_4^{2-}$$

Zinc reacts with the hydronium ions and reduces them to hydrogen.

$$Zn + 2H_3O^+ \rightarrow Zn^{2+} + 2H_2O + H_2\uparrow$$

19. Sodium chloride, an ionic compound, furnishes $Cl^-$ ions with which the $Ag^+$ ions from silver nitrate unite to form the precipitate of silver chloride. Ethyl chloride, ($C_2H_5Cl$), being a covalent compound, does not furnish $Cl^-$ ions and, therefore, does not give precipitate with silver nitrate solution.

20. (*a*) A direct electric currents is used since only if electrons continue moving in the same direction can consistent reactions at each electrode occur.

(*b*) The ions travel under a potential difference to the oppositely charged electrode; positive ions or cations to the cathode, and negative ions or anions to the anode.

(*c*) Oxidation of anions occurs at the anode since the anions give up their electrons, *e.g.*,

$$Cl^- \rightarrow Cl + e^-$$

(*d*) Reduction of cations occurs at the cathode since the cations take up electrons to form neutral atoms; *e.g.*,

$$Na^+ + e^- \rightarrow Na$$

21. Because the constituent ions in the crystal are rigidly fixed in their positions and are not free to move.

24. Strong electrolytes are completely dissociated in solutions. Weak electrolytes, on the other hand, do not dissociate 100 per cent in solutions and an equilibrium exists between the free ions and the non-ionized molecules ($AB \rightleftharpoons A^+ + B^-$). To such a system in equilibrium the law of chemical equilibrium (law of mass action) can be applied.

26. The ionic product of water, $[H^+][OH^-]$, remains unchanged when an acid or a base is dissolved in water. On the addition of an acid, the $H^+$ ion concentration increases and the $OH^-$ ion concentration correspondingly decreases. On the addition of a base, the $OH^-$ ion concentration increases and the $H^+$ ion concentration correspondingly decreases. In either case, the ionic product $[H^+][OH^-]$ has the same constant value ($10^{-14}$ at 25°C).

27. The concentration of $H^+$ ion as also of $OH^-$ ion in pure water is the same, viz., $10^{-7}$ gram-ion per litre.

33. (*a*) Any alkali, *e.g.*, NaOH.

(*b*) Any ammonium salt, *e.g.*, $NH_4Cl$.

(*c*) Common-ion effect.

34. The *p*H of a solution containing both acetic acid and sodium acetate is higher than that of a solution containing the same concentration of acetic acid alone. The reason is that the dissociation of acetic acid, a weak acid, is suppressed in the presence of sodium acetate, by the common-ion effect. As a result, the $H^+$ ion concentration is decreased which means a higher *p*H.

35. (1) The suppression of the dissociation of hydrogen sulphide ($H_2S \rightleftharpoons 2H^+ + S^{2-}$) by using hydrochloric acid is used in separating the sulphides of the metal ions of various groups.

(2) The suppression of the dissociation of ammonium hydroxide by using ammonium chloride is used in separating the hydroxides of the metals of various groups.

38. CaO — increases; KCl — unchanged
$NH_4Cl$ — decreases; $CuSO_4$ — decreases
$CO_2$ — decreases; sodium acetate — increases.

39. Acetic acid is a much weaker acid than hydrochloric acid. Hence, it dissociates to a much smaller extent. A 1M acetic acid solution has, therefore, a much lower concentration of $H^+$ ion than a 1M hydrochloric acid solution.

41. $K_{sp}\ AgBr = [Ag^+][Br^-]$

$K_{sp}\ Ba_3(PO_4)_2 = [Ba^{2+}]^3[PO_4^{3-}]^2$

$K_{sp}\ Ag_2S = [Ag^+]^2[S^{2-}]$

$K_{sp}\ PbCl_2 = [Pb^{2+}][Cl^-]^2$

□ □

# 8

# Chemical Reactions and Energies

**A chemical reaction is always accompanied with the evolution or absorption of energy, most commonly in the form of heat. The relation of energy to chemical changes is important both in theoretical chemistry and in its practical applications. Many chemical reactions, such as those involved in the burning of fuels or the digestion of foods, are more important for the heat released by them than for the formation of new substances.**

**The unit of heat energy used is the calorie, unit symbol cal, which is defined as the quantity of heat required to raise the temperature of one gram of water by 1°C or 1K. Nowadays, it is more common to use joule, unit symbol J, as the unit of energy. These two units are related as follows : 1 calorie = 4·184 joule. Very often the units used are kilo-calorie (=1000 calories) and kilo-joule (=1000 joules); these are symbolized as kcal and kJ respectively. Obviously, 1 kcal = 4·184 kJ.**

## 1. Exothermic and Endothermic Reactions

**1-1. Exothermic reactions.** Many chemical reactions, such as combustion, combination of metals with oxygen, sulphur, or chlorine, neutralization of acids by alkalis, etc., take place with evolution of heat. *Chemical reactions that take place with evolution of heat are called exothermic reactions.* Two such reactions are represented by the equations :

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} + 571{\cdot}8 \text{ kJ}$$
$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(l)} + 694{\cdot}6 \text{ kJ}$$

Exothermic reactions, especially the combustion of various kinds of fuels such as wood, coal, petroleum, etc., are widely used as sources of energy in everyday life and in industry. Once started, exothermic reactions proceed in the absence of any supply of energy from outside. Hydrogen (or, for that matter sulphur, carbon, or any other combustible material) will continue to burn in oxygen with evolution of heat until the supply of either reactant is exhausted.

**1-2. Endothermic reactions.** In many chemical reactions, such as the decomposition of mercuric oxide, combination of nitrogen and oxygen, the interaction of steam and glowing coke, etc., heat is absorbed. *Chemical reactions that take* *place with the absorption of heat are called endothermic reactions.* Chemical equations for some endothermic reactions are given below :

$$2HgO_{(s)} \rightarrow 2Hg_{(l)} + O_{2(g)} - 180{\cdot}4 \text{ kJ}$$
$$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)} - 181{\cdot}0 \text{ kJ}$$
$$H_2O_{(g)} + C_{(s)} \rightarrow H_{2(g)} + CO_{(g)} - 131{\cdot}2 \text{ kJ}$$

Endothermic reactions require a continuous supply of heat from outside to keep them going, and stop immediately if heating is discontinued. For example, the decomposition of mercuric oxide into mercury and oxygen will continue only so long as the compound is heated.

It must be noted that *any reaction that is exothermic when it proceeds in one direction is endothermic when it proceeds in the reverse direction*. For example, the reaction $H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$ is exothermic and is accompanied with the evolution of 285·9 kJ of heat energy per mole. The reverse reaction $H_2O_{(l)} \rightarrow H_{2(g)} + \frac{1}{2} O_{2(g)}$ is endothermic and is accompanied with the absorption of 285·9 kJ of heat energy per mole (Fig. 8-1). In general, if a certain quantity of heat is evolved (or absorbed) during the formation of a chemical compound from simple substances, the same quantity of heat will be absorbed (or evolved) when that substance is decomposed into its simple substances.

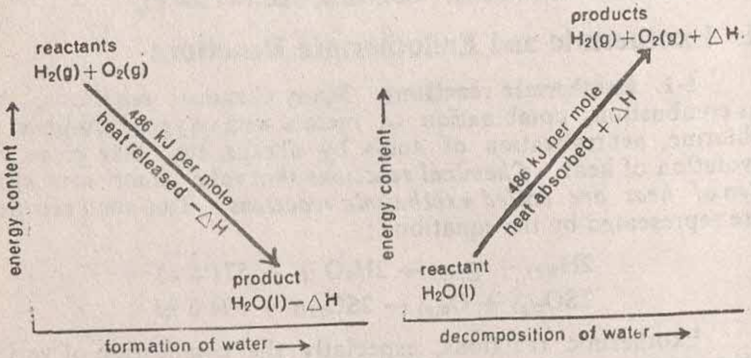

Fig. 8-1. Heat evolved per mole of product in the formation of water (left) is exactly equal to heat absorbed in the decomposition of the water (right).

**1-3. Exothermic and endothermic compounds.** Chemical compounds formed from simple substances with the evolution of heat are called *exothermic compounds*; those formed with the absorption of heat are termed *endothermic compounds*. Endothermic compounds are much rarer than the exothermic, form from simple substances only at high temperatures, and decompose with relatively greater ease. The exothermic compounds, on the contrary, usually form at low or moderate temperatures, and are more stable than the endothermic compounds.

**1-4. Law of Conservation of energy.** Energy may be evolved or absorbed in a chemical reaction, but the total energy of the reacting system and its surroundings remains constant. This is a corollary of the wider generalization known as the law of conservation of energy according to which '*energy is neither created nor destroyed*'.

## 2. Thermochemical Equations

Chemical equations in which the quantity of heat evolved or absorbed during the reaction is indicated are called *thermochemical equations*. The various conventions followed with regard to thermochemical equations are as follows :

(1) The heat evolved or absorbed in a reaction is affected by the physical state of the reacting substances, which are therefore specified using the symbols (*g*), (*l*), and (*s*). These symbols are placed alongside the chemical formulae to indicate gaseous, liquid, and solid states respectively.

(2) In case of elements which exhibits allotropy, the name of the allotropic modification is mentioned, *e.g.*, C (*graphite*) (*s*), C(*diamond*)(*s*), S(*rhombic*)(*s*), S(Monoclinic)(*s*) etc. This is necessary since different allotropes of the same element have different energies.

(3) The substances in aqueous solutions are specified using the symbol *aq*, *e.g.*, NaCl(*aq*) stands for an aqueous solution of sodium chloride. It also signifies that the quantity of water is so large that no further heat change would occur upon addition of more water.

(4) In the older convention, the heat evolved or absorbed in the reaction was shown with the positive sign and negative sign respectively on the right hand side of the equation, as in the equations given on pages 213 and 214. In modern convention, the heat evolved or absorbed in the reaction is represented as the difference in ***heat content*** between products and reactants, denoted by the symbol $\triangle H$ (delta H). The symbol $\triangle H$ is placed at the end of the equation for the reaction. For an exothermic reaction, $\triangle H$ has a negative value : $\triangle H = -x$ kJ or $-x$ kcal. The minus sign indicates that the heat content of the products is less than the heat contents of the reactants, or that there has been a loss in heat content. Thus, the thermochemical equation for the formation of water is :

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} \quad \triangle H = -571{\cdot}8 \text{ kJ}$$

If the reaction is endothermic, $\triangle H$ has a positive value : $\triangle H = +x$ kJ or $+x$ kcal. The plus sign indicates that the heat content of the products is more than the heat content of the reactants, or that there has been a gain in the heat content. Thus, the thermochemical equation for the decomposition of water is :

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)} \quad \triangle = +571{\cdot}8 \text{ kJ}$$

In other words, △H with a negative value signifies evolution of heat ; △H with a positive value signifies absorption of heat.

It may also be noted that a thermochemical equation can be reversed by merely changing the sign of the heat quantity. Thus, the equation

$$H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)} \quad \triangle H = -14\text{kJ}$$

may be written as

$$2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)} \quad \triangle H = 14\text{kJ}$$

(5) If necessary, the temperature and pressure at which the reaction proceeds are indicated as subscript and superscript respectively on △H as in the following example :

$$C(\textit{graphite}) + O_{2(g)} \rightarrow CO_{2(g)} \ ; \ \triangle H^{760\text{mm}}_{298°\text{K}} = -393{\cdot}5 \text{ kJ}$$

**2-1. Calculations based on thermochemical equations.** The amount of heat involved in a thermochemical equation is part of the total equation, like the other products and reactants, and is handled stoichiometrically in calculations. Also, thermochemical equations can be handled like algebraic equations. For example, from the equation

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} \ ; \ \triangle H = -571{\cdot}8\text{kJ}$$

we can derive the following relationships :

(1) Stoichiometric relationships between moles of products or reactants and amount of heat, such as

$$2 \text{ moles } H_2 = -571{\cdot}8 \text{ kJ, or, } 2 \text{ moles } H_2O = -571{\cdot}8 \text{ kJ}$$

(2) For the reverse reaction, 571·8 kJ of heat are absorbed (an endothermic reaction)

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)} \ ; \ \triangle H = 571{\cdot}8 \text{ kJ}$$

(3) Dividing the total equation by 2, the following equation is derived :

$$H_{2(g)} + \tfrac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)} \ ; \ \triangle H = -285{\cdot}9 \text{ kJ}$$

Calculations based on thermochemical equations are illustrated in the following two examples It must be remembered that in order to make the heat effects of various reactions comparable, thermochemical equations and calculations usually relate to standard conditions : one mole of a compound, a temperature of 25°C (Or 298°K), and 1 atm. pressure.

**Example 2-1**. *The heat evolved in the combustion of glucose is shown in the following equation :*

$$\underset{\text{(glucose)}}{C_6H_{12}O_{6(s)}} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(g)} \ ; \ \triangle = -2840 \text{ kJ}$$

*How much energy will be required for the production of 1·08 g of glucose.*

**Solution**. Glucose will, obviously, be produced by the reverse reaction which can be represented by the equation

$$6CO_{2(g)}+6H_2O_{(g)} \rightarrow C_6H_{12}O_{6(g)} + 6O_{2(g)}\ ;\ \triangle H = 2840\ kJ$$

This equation refers to 1 mole of glucose, *i.e.*, 180 g of glucose. According to this equation.

Production of 180 g of glucose requires 2840 *kJ* of energy.

$\therefore$ Production of 1·08 g of glucose will require $\frac{2840\ kJ}{180\ g} \times 1{\cdot}08g$

**=17·04 kJ of energy.**

**Example 2-2**. *The heat evolved in the combustion of methane is given by the following equation :*

$$CH_{4(g)}+2O_{2(g)} \rightarrow CO_{2(g)}+2H_2O_{(l)}\ ;\ \triangle H = -890{\cdot}3\ kJ$$

(*a*) *Haw many grams of methane should be burnt to produce 4451·50 kJ of heat ?*

(*b*) *How many grams of CO₂would be formed when methane burns to give 4451·50 kJ of heat ?*

**Solution**. The equation refers to 1 mole or 16g of methane ($CH_4$).

(*a*) According to the equation—

890·3 kJ of heat is produced by burning 16g of methane.

$\therefore$ 4451·5 kJ of heat will be produced by burning

$$\frac{16g \times 4451{\cdot}5\ kJ}{890{\cdot}3\ kJ} = 80g \text{ of methane}$$

(*b*) According to the equation—

890·3 kJ of heat liberated corresponds to 1 mole or 44g of $CO_2$.

$\therefore$ 4451·5 kJ of heat corresponds to $\frac{44g \times 890{\cdot}3\ kJ}{4451{\cdot}5\ kJ}$

$= 220$ g of $CO_2$

## 3. Heat of Reaction

The quantity of heat given out or absorbed when the number of moles of reactants indicated by the chemical equation of the reaction have completely reacted is called the heat of reaction. It is usually denoted by the symbol $\triangle H_r$. Thus, the quantities of heat shown with the foregoing thermochemical equations represent the heat of the corresponding reaction. For example, the equation

$$C_{(s)}+O_{2(g)} \rightarrow CO_{2(g)};\ \triangle H = -393{\cdot}5\ kJ$$

shows that the heat of reaction involving the combination of one mole of carbon and one mole of oxygen is −393·5 kJ.

It may be recalled that the heat of a reaction is equal to the difference in the total heat content of the products and the total heat content of the reactants. That is,

$$\triangle H_r = \Sigma \triangle H \text{ products} - \Sigma \triangle H \text{ reactants}$$

In this equation, the symbol $\Sigma$ means 'the sum of'.

## 4. Heat of Formation

The quantity of heat evolved or absorbed when one mole of a compound is formed from its elements in their normal state* is called its heat of formation. It is denoted by the symbol $\triangle H_f$. From the following equations

$$C_{(graphite)} + 2H_{2(g)} \rightarrow CH_{4(g)};\ \triangle H = -74{\cdot}8 \text{ kJ}$$

and, $$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)};\ \triangle H = -393{\cdot}5 \text{ kJ}$$

the heat of formation of methane is $-74{\cdot}8$ kJ and of carbon dioxide $-393{\cdot}5$ kJ

For the purpose of thermochemical calculations, the heat content or heat of formation of an element when it is in its standard state is taken to be zero. Though not correct in reality, it is an extremely useful convention as the changes in heat content are significant rather than the absolute heat contents of reactants and products. Thus, the heat of formation, $\triangle H_f$, of a compound becomes its heat content on a scale on which the heat contents of elements are zero. Therefore, if the $H_f$ values of reactants and products are known, the $\triangle H_r$ for the reaction can be calculated from the relationship

$$\triangle H_r = \Sigma \triangle H_f \text{ products} - \Sigma \triangle H_f \text{ reactants.}$$

This is illustrated in the following example :

**Example 4-1**. *The heats of formation of $CO_{2(g)}$, $H_2O_{(l)}$, and $CH_{4(g)}$ are $-393{\cdot}5$ kJ mol$^{-1}$, $-285{\cdot}9$ kJ mol$^{-1}$, and $-74{\cdot}8$ kJ mol$^{-1}$ respectively. Calculate the heat of the reaction represented by the equation*

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$$

**Solution,**

$$\begin{aligned}\triangle H_r &= \Sigma \triangle H_f \text{ products} - \Sigma \triangle H_f \text{ reactants}\\ &= [\triangle H_f CO_{2(g)} + \triangle H_f H_2O_{(l)} - [\triangle H_f CH_{4(g)} + \triangle H_f O_{2(g)}]\\ &= [-393{\cdot}5 + 2\,(-285{\cdot}9)] - [-74{\cdot}8 + 2\times 0] \text{ kJ}\\ &= [-393{\cdot}5 - 571{\cdot}8] - [-74{\cdot}8 + 0] \text{ kJ}\\ &= -393{\cdot}5 - 571{\cdot}8 + 74{\cdot}8 \text{ kJ}\\ &= -890{\cdot}5 \text{ kJ}\end{aligned}$$

$\therefore$ Heat of the reaction in question is 890·5 kJ.

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*The normal or standard state is defined as the most stable form of an element, *e.g.*, C (graphite) for carbon and $O_{2(g)}$ for oxygen.

**4-1. Heat of formation and stability.** Heat of formation is the heat evolved or absorbed when a mole of compound is formed from its constituent elements. However, 1 mole of every compound contains the same number of molecules, viz., $6{\cdot}02 \times 10^{23}$ (Avogadro number). Now, the heat of formation of carbon dioxide is −393·5 kJ per mole and that of water (liquid) is −285·9 kJ per mole. This means that more heat is given off in the formation of a molecule of carbon dioxide than in the formation of a molecule of water. Since the heat contents of all elements are zero, each molecule of carbon dioxide contains less energy than a molecule of water. Because they contain less energy, the $CO_2$ molecules are more stable than the $H_2O$ molecules. Or, more energy will be required to decompose the $CO_2$ molecules than the $H_2O$ molecules.

Nitrogen and oxygen combine at the very high temperature of an electric arc to form nitric oxide. NO. The heat of formation of nitric oxide is +89·9 kJ $mol^{-1}$. That is, 89·9 kJ of heat is absorbed in the formation of one mole of nitric oxide. This indicates that nitric oxide is relatively unstable, and it actually is. Some other compounds with positive heats of formation are acetylene, carbon disulphide, hydrogen peroxide, and the oxides of nitrogen. All of these are relatively unstable.

In general, the higher the negative heat of formation, the more stable the compound is. Conversely, the lower the negative heat of formation or higher the positive heat of formation, the more unstable the compound is. Compounds with very high positive heats of formation are extremely unstable and tend to decompose explosively.

## 5. Heat of Combustion

The amount of heat evolved by one mole of a substance when it is completely burnt in air or oxygen is termed its heat of combustion. From the equation

$$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{(g)} + 3H_2O_{(l)};\ \triangle H = -1365{\cdot}6\ kJ$$

the heat of combustion of ethyl alcohol ($C_2H_5OH$) is −1365·6 kJ $mol^{-1}$. That is, 1365·6 kJ of heat is evolved when one mole of ethyl alcohol (=46 g) is completely burnt in oxygen.

Heat of combustion (as also heat of formation) is defined in terms of one mole of a compound. Therefore in calculating the heat of combustion (or heat of formation) of a substance, it should be represented as one mole in the chemical equation. Such an equation, if not already so, can be derived by dividing the whole equation by a suitable whole number For example, the equation for the burning of acetylene in oxygen is

$$2C_2H_{2(g)} + 5O_{2(g)} \rightarrow 4CO_{2(g)} + 2H_2O_{(l)};\ \triangle H = -259{\cdot}4\ kJ$$

For calculating the heat of combustion of acetylene, this equation is divided by two to obtain

$$C_2H_{2(g)} + 2\frac{1}{2}O_{2(g)} \rightarrow 2CO_{2(g)} + H_2O_{(l)};\ \triangle H = -129.7 kJ$$

from which the heat of combustion of acetylene is $-129.7$ kJ mol$^{-1}$.

It should be noted that the heats of combustion of elements such as carbon, sulphur, and hydrogen represent the heat of formation of their oxides—carbon dioxide, sulphur dioxide, and water respectively.

$$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)};\ \triangle H = -393.5 \text{ kJ}$$

$$S_{(rhombic)} + O_{2(g)} \rightarrow SO_{2(g)};\ \triangle H = -296.6 \text{ kJ}$$

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}:\ \triangle H = -285.9 \text{ kJ}$$

Thus, from the first equation, $-393.5$ kJ represents the heat of combustion of carbon per mole as well as the heat of formation of carbon dioxide. It also gives the heat of reaction as represented by the equation.

## 6. Heat of Solution

Heat is either evolved or absorbed when a substance dissolves in a solvent. The quantity of heat evolved or absorbed when one mole of a substance is dissolved in such a large volume of the solvent that further addition of solvent causes no further heat change is called the heat of solution (of that substance in that solvent). When such dilute solutions are made in water, this fact is indicated by using the symbol 'aq'. Thus, from the equation

$$Na^+Cl^- + aq \rightarrow Na^+Cl^- \text{ (aq)};\ \Delta H = +5.0 \text{ kJ}$$

the heat of solution of sodium chloride in water is 5.0 kJ mol$^{-1}$. That is, 5.0 kJ of heat is absorbed when 1 mole of sodium chloride (=58.5 *g*) is dissolved in a large excess of water.

## 7. Heat of Neutralization

Heat is evolved when in aqueous solution an acid is neutralized by a base, and *vice versa*. The heat of neutralization is the amount of heat evolved when one mole of an acid is neutralized by one mole of a base in dilute solutions such that further addition of water would not cause any rise in temperature.

The neutralization reactions involve essentially the reaction between the $H^+$ (aq) from the acid and the $OH^-$ (aq) from the base. For example,

$$Na^+OH^-_{(aq)} + H^+Cl^-_{(aq)} \rightarrow Na^+Cl^-_{(aq)} + H_2O_{(l)};\ \triangle H = -57 \text{ kJ}$$

or, cancelling out the common ion on both sides.

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)};\ \Delta H = -57 \text{kJ}$$

As such, the heat of neutralization for any strong acid (*e.g.*, $H_2SO_4$.HCl, $HNO_3$) and any strong base [*e.g.*, NaOH, KOH, $Ba(OH)_2$] is $-57$kJ or 13.6 kcal.

However, if either the acid or the base is weak, or both are weak, the heat of neutralization is less than −57 kJ mole$^{-1}$. This is because some energy is used up in causing the ionization of the weak acid or weak base. Thus, when acetic acid is neutralized by NaOH, the heat of neutralization has a lower value, −56·1 kJ mol$^{-1}$. The heats of neutralization for a HCN, H.COOH, and $NH_4OH$ are given below :

$$HCN_{(aq)}+NaOH_{(aq)} \rightarrow NaCN_{(aq)}+H_2O_{(l)};\ \triangle H=-54{\cdot}0\ kJ$$

$$H.COOH_{(aq)}+NH_4OH_{(aq)} \rightarrow HCOONH_{4(aq)}+H_2O_{(l)};\triangle H=-49{\cdot}8\ kJ.$$

$$HCl_{(aq)}+NH_4ON_{(aq)} \rightarrow NH_4Cl_{(aq)}+H_2O_{(l)};\ \triangle H=-51{\cdot}5\ kJ$$

## 8. Hess's Law

On the basis of his experimental measurements of heats of reactions, G.H. Hess in 1840 proposed the following generalization :

*The heat evolved or absorbed in a reaction is independent of any intermediate steps and depends only upon the initial reactants and final products of the reaction.*

This generalization has been found to be applicable to every reaction that has been tested, and is now called the *Hess's law of constant heat summation.*

Suppose $H_1$ represents the heat content of the reactants and $H_2$ the heat content of the products. The net change in the reaction is $H_2-H_1$, or $\triangle H$, and this difference will be the same for the overall process whether it is accomplished in one step or several steps Let there be a substance A that can be converted into another substance B either directly, when the heat of reaction is $Q_1$ kJ, or indirectly by way of substances X and Y when the

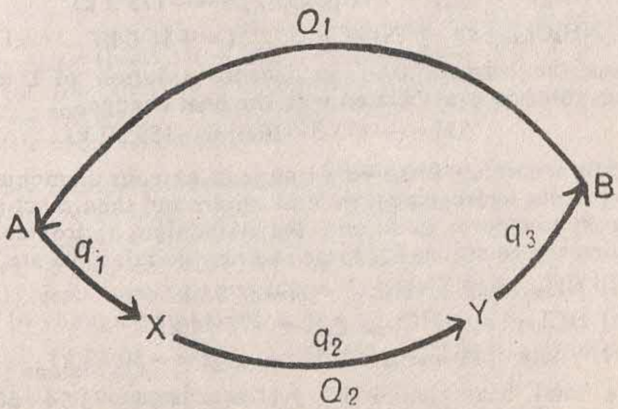

Fig. 8-2. Hess's law illustrated.

heats of reaction of the three steps are $q_1$ kJ, $q_2$ kJ, and $q_3$ kJ respectively.

$$A \rightarrow B;\ \Delta H = Q_1 \text{ kJ}$$
$$A \rightarrow X;\ \Delta H = q_1 \text{ kJ}$$
$$B \rightarrow Y:\ \Delta H = q_2 \text{ kJ}$$
$$Y \rightarrow B;\ \Delta H = q_3 \text{ kJ}$$

Then according to Hess's law the heat of reaction in going from A to B is the same whether the change occurs directly or through the series of separate steps. That is. $Q_1 = q_1 + q_2 + q_3$.

**10·1. Theoretical deduction of Hess's law.** Suppose a given chemical system A can be changed into another sytem B in two ways : (*i*) directly, when the heat liberated is $Q_1$ kJ, and (*ii*) in three steps. *viz.* $A \rightarrow X$, $X \rightarrow Y$ and $Y \rightarrow Z$ in which the heat liberated is $q_1$ kJ, $q_2$ kJ, and $q_3$ kJ, respectively (Fig. 8-3). Let $q_1 + q_2 + q_3 = Q_2$ kJ. According to Hess's law, $Q_1$ must be equal to $Q_2$. If not, let $Q_2 > Q_1$. Then, in converting A to B through X and Y and then reconverting it directly into A there would be a net gain of $(Q_2 - Q_1)$ kJ of heat. By repeating the cyclical process an unlimited amount of heat could be produced without doing any work or using any other form of energy This is against the law of conservation of energy. Hence, $Q_1$ must be equal to $Q_2$ as required by Hess's law.

**8-2. Verification of Hess's law.** Hess's law can be verified by preparing an aqueous solution of ammonium chloride in the following two different ways and measuring the heats of reactions involved :

(1) By reacting 1 mole each of gaseous ammonia and gaseous hydrogen chloride and then dissolving the 1 mole of solid ammonium chloride formed in water. The thermochemical equations are :

(*i*) $NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)};\ \Delta H = -175\cdot3 \text{ kJ}$

(*ii*) $NH_4Cl_{(s)} + aq \rightarrow NH_4Cl_{(aq)};\ \Delta H = +16\cdot0 \text{ kJ}$

Thus, the formation of an aqueous solution of 1 mole of ammonium chloride is associated with the heat change,

$$\Delta H = (-175\cdot3 + 16\cdot0) = -159\cdot30 \text{ kJ}$$

(2) By separately dissolving 1 mole of gaseous ammonia and 1 mole of gaseous hydrogen chloride in water, and then reacting the resulting hydrochloric acid and the ammonium hydroxide. The thermochemical equations for these exothermic relations are :

(*i*) $NH_{3(g)} + aq \rightarrow NH_{3(aq)};\ \Delta H = 34\cdot94 \text{ kJ}$

(*ii*) $HCl_{(g)} + aq \rightarrow HCl_{(aq)}\ \Delta H = -73\cdot74 \text{ kJ}$

(*iii*) $NH_{3(aq)} + HCl_{(aq)} \rightarrow NH_4Cl_{(aq)};\ \Delta H = -50\cdot62 \text{ kJ}$

The total heat change is $\Delta H = (-34\cdot94 - 73\cdot74 - 50\cdot62) = -159\cdot30$ kJ. This is the same as in the formation of $NH_4Cl_{(aq)}$ by the other method in different steps.

**8-3 Importance of Hess's law.** The practical importance of Hess's law lies in the fact that it justifies the addition or subtraction of heat changes in reactions in an algebraic manner. This makes it possible to calculate heat changes in cases where they cannot be measured directly for some reason or other For example, the heat of formation of carbon monoxide $\Delta H_f CO$, cannot be determined directly by experiment as carbon (graphite), when burnt in oxygen, forms carbon dioxide and not carbon dioxide However, $\Delta H_f CO$ can be calculated from the heat of formation of carbon dioxide from carbon and oxygen and the heat of combustion of carbon monoxide, both of which can be easily determined by experiment. The method of calculation is explained below :

Combustion of carbon in oxygen is represented by the thermochemical equation

$$C(\text{graphite}) + O_{2(g)} \rightarrow CO_{2(g)};\ \Delta H_1 = -396 \text{ kJ}$$

We break this reaction in two stages, assuming that the carbon burns to first form carbon monoxide, which then burns to give carbon dioxide. The thermochemical equations for these stages are :

$$C(\textit{graphite}) + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{(g)};\ \Delta H = \Delta H_f CO$$

$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{2(g)};\ \Delta H_2 = -285{\cdot}5 \text{ kJ}$$

According to Hess's law, the heat change in the formation of $CO_2$ is the same, whether formed direct from carbon and oxygen or through the intermediate formation of CO. That is,

$$\Delta H_1 = \Delta H_f CO + \Delta H_2$$

Or,

$$\begin{aligned}\Delta H_f CO &= \Delta H_1 - \Delta H_2\\ &= -396 - (-285{\cdot}5) = -110{\cdot}5 \text{ kJ.}\end{aligned}$$

Therefore, the heat of formation of carbon monoxide from carbon and oxygen is, $\Delta H_f = -110{\cdot}5$ kJ.

These calculations show that when carbon burns to carbon monoxide ($\Delta H = -110{\cdot}5$ kJ), it evolves about only 31 per cent of the heat liberated by its complete combustion to carbon dioxide ($\Delta H = -396{\cdot}0$ kJ) Hence, the economic importance of ensuring complete combustion of fuels.

**8-4 Calculations based on Hess's law.** In the calculations based on Hess's law, it must be appreciated that thermochemical equations may be manipulated according to the conventions of algebra. Thus, the signs may be changed by multiplying all terms by $-1$, terms may be transposed from one side of the equation to other by changing signs, etc.

**Example 8-1.** *The heat of combustion of graphite is $-395$ kJ mol$^{-1}$ and of diamond $-393{\cdot}5$ kJ mol$^{-1}$.*

(*a*) *What is the* $\Delta$H *when diamond is formed from graphite* ?

*(b) Is the change graphite→diamond endothermic or exothermic ?*

*(c) Which is more stable, diamond or graphite ?*

**Solution**. (*a*) The relevant thermochemical equations are :

$C(graphite)+O_{2(g)} \rightarrow CO_{2(g)}$; $\triangle H=-395{\cdot}0$ kJ

$C(diamond)+O_{2(g)} \rightarrow CO_{2(g)}$; $\triangle H=-393{\cdot}5$ kJ

Applying Hess's law by substracting the first equation from the second

$C(diamond)-C(graphite) \rightarrow 0$; $\triangle H=-1{\cdot}5$ kJ ...(1)

Or, $C(diamond) \rightarrow C(graphite)$; $\triangle H=-1{\cdot}5$ kJ ...(2)

∴ $\triangle H$ for the formation of diamond from graphite is **−1·5 kJ**

(*b*) Reserving equation (2) derived above,

$C(graphite) \rightarrow C(diamond)$; $\triangle H=+1{\cdot}5$ kJ

∴ Heat is absorbed when graphite is changed to diamond.

(*c*) Graphite is somewhat more stable than diamond since it contains 1·5 kJ less energy per mole than diamond.

**Example 8-2**. *The heat of combustion of methane is −890·5 kJ mole⁻¹. The heats of formation of* $CO_{2(g)}$ *and* $H_2O_{(l)}$ *are −393·5 kJ mole⁻¹ and −285·9kJ mole⁻¹ respectively. Calculate the heat of formation of methane.*

**Solution**. The relevant thermochemical equations are :

(*i*) $CH_{4(g)}+2O_{2(g)} \rightarrow CO_{2(g)}+2H_2O$; $\triangle H=-890{\cdot}5$ kJ

(*ii*) $C_{(s)}+O_{2(g)} \rightarrow CO_{2(g)}$; $\triangle H=-393{\cdot}5$ kJ

(*iii*) $H_{2(g)}+\frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$; $\triangle H=-285{\cdot}9$ kJ

The heat of formation of methane may be found from the hypothetical thermochemical equation

$C_{(s)}+2H_{2(g)} \rightarrow CH_{4(g)}$; $\triangle H=?$

This equation can be derived by reversing equation (*i*), multiplying equation (*iii*) by 2, and then adding the resulting equations with equation (*ii*). That is

$$
\begin{array}{ll}
CO_{2(g)}+2H_2O \rightarrow CH_{4(g)}+2O_{2(g)}; & \triangle H=+890{\cdot}5 \text{ kJ} \\
2H_{2(g)}+O_{2(g)} \rightarrow 2H_2O_{(l)}; & \triangle H=-571{\cdot}8 \text{ kJ} \\
C_{(s)}+O_{2(g)} \rightarrow CO_{2(g)}; & \triangle H=-393{\cdot}5 \text{ kJ} \\
\hline
C_{(s)}+2H_{2(g)} \rightarrow CH_{4(g)}; & \triangle H=-74{\cdot}8 \text{ kJ}
\end{array}
$$

∴ The heat of formation of methane, $\Delta H=-74{\cdot}8$ kJ

**Example 8-3**. *Calculate the heat of formation* ($\triangle H_f$) *of caustic soda from the following data.*

(*i*) $Na+water=NaOH\ aq)+\frac{1}{2}H_2$; $\triangle H=-98{,}000$ cal (*ii*) $H_2(g)+\frac{1}{2}O_2(g)=H_2O(g)$ ; $\triangle H=-68{,}380$ *cal*

(*iii*) $NaOH(s)+water=NaOH(aq)$ ; $\triangle H=-13{,}300$ *cal*

**Solution.** The required equation is

$$Na+\tfrac{1}{2}H_2+\tfrac{1}{2}O_2 \rightarrow NaOH \; ; \; \triangle H=?$$

This hypothetical equation can be derived by

(*a*) keeping equation (*i*) and (*ii*) as such (to have Na, $\frac{1}{2}O_2$, and $\frac{1}{2}H_2$ as reactants),

(*b*) reversing equation (*iii*) (to have NaOH as product), and

(*c*) adding the three equations algebraically

$$\begin{array}{ll}
Na+water \rightarrow NaOH_{(aq)}+\tfrac{1}{2}H_2, & \triangle H_1=-98{,}000 \text{ cal} \\
H_2(g)+\tfrac{1}{2}O_2(g) \rightarrow H_2O(g), & \triangle H_2=-68{,}380 \text{ cal} \\
NaOH_{(aq)} \rightarrow NaOH(s)+water \; ; & \triangle H_3=-13{,}300 \text{ cal} \\
\hline
Na+\tfrac{1}{2}H_2+\tfrac{1}{2}O_2 \rightarrow NaOH \; ; & \triangle H_f=-153{,}080 \text{ cal}
\end{array}$$

∴ The heat of formation of *caustic soda* $\triangle H_f=$**153,080** cal

**Example 8-4.** *Calculate the heat of the reaction*

Given— $CO_{2(g)}+H_{2(g)} \rightarrow CO_{(g)}+H_2O_{(g)}$

$$\begin{array}{ll}
(i)\; C_{(s)}+\tfrac{1}{2}O_{2(g)} \rightarrow CO_{(g)}; & \triangle H=-26{\cdot}4 \text{ kcal} \\
(ii)\; C_{(s)}+O_{2(g)} \rightarrow CO_{2(g)}; & \triangle H=-94{\cdot}1 \text{ kcal} \\
(iii)\; H_{2(g)}+\tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}; & \triangle H=-57{\cdot}8 \text{ kcal}
\end{array}$$

**Solution.** The required equation is derived by reversing equation (*ii*) so that $CO_2$ is a reactant, keeping equation (*i*) and (*iii*) as such, and then adding up the three equation algebraically. That is

$$\begin{array}{ll}
C_{(s)}+\tfrac{1}{2}O_{2(g)} \rightarrow CO_{(g)}; & \triangle H=-26{\cdot}4 \text{ kcal} \\
CO_{2(g)} \rightarrow C_{(s)}+O_{2(g)}; & \triangle H=+94{\cdot}1 \text{ kcal} \\
H_{2(g)}+\tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)} & \triangle H=-57{\cdot}8 \text{ kcal} \\
\hline
CO_{2(g)}+H_{2(g)} \rightarrow CO_{(g)}+H_2O_{(g)}; & \triangle H=9{\cdot}9 \text{ kcal}
\end{array}$$

The heat of reaction is **9·9 k cal.**

### Questions

1. (*a*) Define the terms exothermic reactions and endothermic reactions.

(*b*) Differentiate between exothermic compounds and endothermic compounds. Which kinds of compounds are more reactive ?

2. The formation of carbon disulphide ($CS_2$) from carbon and sulphur is represented by the equation

$$C_{(s)}+2S_{(s)} \rightarrow CS_{2(g)}; \quad \triangle H=+120 \text{ kJ}$$

(*a*) Is the reaction exothermic or endothermic ? Justify your answer.

(*b*) What is the significance of the letters (*s*) and (g) in the equation ?

3. (*a*) When 1 mole of graphite is completely oxidized to carbon dioxide at 298°K and 760 mm pressure, 393·5 kJ of heat is liberated. Write a thermochemical equation for this change.

(*b*) Write thermochemical equation using $\Delta H$ for the dissociation of 1 mole of gaseous chlorine into atoms which is accompanied by the absorption of 242·7 kJ of heat.

(*c*) Given $\frac{1}{2}H_{2(g)}+\frac{1}{2}Br_{2(g)} \rightarrow HBr_{(g)}$; $\Delta H=-36$ kJ. Rewrite the equation for one mole of hydrogen gas including the heat effect as a term in the equation.

(*d*) Given $2C_2H_{2(g)}+5O_{2(g)} \rightarrow 4CO_{2(g)}+2H_2O_{(l)}+2594$ kJ. Rewrite the equation for one mole of $C_2H_2$ using the $\Delta H$ notation for the heat effect.

3. Write brief explanatory notes on any two of the following giving a suitable example in each case :

(1) Heat of reaction.

(2) Heat of formation.

(3) Heat of combustion.

(4) Heat of solution.

(5) Heat of neutralization.

5. (*a*) The heats of formation of the various hydrogen halides are as follows : $\Delta H_f HF=-267{\cdot}8$ kJ; $\Delta H_f HCl=-92{\cdot}0$ kJ, $\Delta H_f HBr=-36{\cdot}4$ kJ, and $\Delta H_f HI=+25{\cdot}1$ kJ. Indicate which halogen halide is the the most stable and which one is easiest to decompose.

(*b*) Justify your answer.

6. Explain the reason for the following :

(*a*) The heat of neutralization of any strong acid and any strong base is nearly the same.

(*b*) The heat of neutralization of a weak acid and a weak base is lower than that of a strong acid and a strong base.

7. (*a*) State Hess's law of constant heat summation.

(*b*) Describe by a suitable example how you can experimentally verify Hess's law.

8. (*a*) Deduce Hess's law on the basis of the law of conservation of energy.

(*b*) What is the practical importance of Hess's law ?

## Key

1. (*b*) Endothermic compounds are more reactive.

2. (*a*) The reaction is endothermic because the heat content of the product is less than that of the products and so 120 kJ of heat is absorbed in the reaction.

(*b*) (*s*) stands for solids; (*g*) for gas.

3. (*a*) $C_{(graphite)}+O_{2(g)} \rightarrow CO_{2(g)};\ \triangle H^{760mm}_{298^\circ k} = -393{\cdot}5$ kJ

(*b*) $Cl_{2(g)} \rightarrow 2Cl_{(g)};\ \triangle H = 242{\cdot}7$ kJ.

(*c*) $H_{2(g)}+Br_{2(g)} \rightarrow 2HBr;\ \Delta H = +72$ kJ.

(*d*) $C_2H_{2(g)}+\frac{5}{2}O_{2(g)} \rightarrow 2CO_{2(g)}+H_2O_{(l)};\ \triangle H = -2594$ kJ

5. HF is the most stable hydrogen halide; HI is the easiest to decompose.

(*b*) Since maximum quantity of heat is liberated in the formation of HF molecules, they contain the least energy and are therefore the most stable. The reverse is true for the HI molecules.

### Problems

1. The heat evolved in the combustion of benzene is given by the equation—

$2C_6H_{6(l)}+15O_{2(g)} \rightarrow 12\ CO_{2(g)}+6H_2O_{(l)};\ \triangle H = -6688$ kJ
What weight of benzene will be required to be completely burnt in order to produce 334·4 kJ of heat ?

(**Ans**. 7·8 *g*)

2. Calculate $\triangle H_f$ of carbon monoxide from the following reaction :

$$2C_{(s)}+O_{2(g)} \rightarrow 2CO_{(g)};\ \triangle H = -221\ \text{kJ}$$

(**Ans.** 110 kJ $mol^{-1}$)

3. The heat of formation water is $-286{\cdot}3$ kJ $mol^{-1}$.

$$H_{2(g)}+\tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)};\ \triangle H = -286{\cdot}3\ \text{kJ}$$

How much heat will be liberated upon decomposing 90g of water ? (**Ans.** 1413·5 kJ)

4. Calculate the heat of formation of carbon disulphide if the heats of combustion of carbon, sulphur, and carbon disulphide −394·6 kJ, −298·7 kJ, and −1109 kJ respectively.

(**Ans.** $\Delta H_f = +117$ kJ)

5. Calculate the heat of formation of liquid ethanol ($C_2H_5OH$) at 298 K from the following heats of combustion at the same temperature :

(*i*) $C_2H_5OH_{(l)}+3O_{2(g)} \rightarrow 2CO_{2(g)}+3H_2O_{(l)};\ \triangle H = -1368$ kJ

(*ii*) $C_{(s)}+O_{2(g)} \rightarrow CO_{2(g)};\ \Delta H = -393{\cdot}2$ kJ

(*iii*) $H_{2(g)}+\frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)};\ \triangle H = -286{\cdot}3$ kJ

(**Ans.** $\triangle H_f = -277{\cdot}3$ kJ)

6. Calculate the heat of formation ($\triangle H_f$) of carbon disulphide, given that the heats of combustion ($\triangle H$) of $CS_2$, carbon, and sulphur are −265,100 cal, −94,300 cal, and −71,080 cal respectively ? (**Ans.** $\triangle H_f = 28{,}640$ cal)

[**Hint.** Reverse equation (*i*), multiply **equation** (*iii*) by **2, keep** equation (*ii*) as such, and add up.]

7. Calculate the heat of formation ($\triangle H_f$) of ethyl acetate from ethyl alcohol and acetic acid being given that the heat of combustion of ethyl alcohol is 34,000 cal, of acetic acid is −21,000 cal, and of ethyl acetate is −55,400 cal.

(**Ans.** $\triangle H_f = +400$ cal)

[**Hint.** The given thermochemical equations are :

(*i*) $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$; $\triangle H = -34{,}000$ cal

(*ii*) $CH_3.COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O$; $\triangle H = -21{,}000$ cal

(*iii*) $CH_3.COOC_2H_5 + 5O_2 \rightarrow 4CO_2 + 4H_2O$; $\triangle H = -55{,}400$ cal
ethyl acetate.

Keep equation (*i*) and (*ii*) as such, reverse equation (*iii*) and add up to obtain the required equation

$$C_2H_5OH + CH_3.COOH \rightarrow CH_3.COOC_2H_5 + H_2O;\ \triangle H = \quad ?$$

□ □

# PART 2

# INORGANIC CHEMISTRY

# 9

# Elements of Group IIA

## (Magnesium and Calcium)

The group IIA of the periodic table is comprised of six elements : beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra), the last named being a naturally occuring radioactive element. None of these elements occur in nature in the free state. With the exception of beryllium, these elements have lower melting and boiling points than most metals, and except radium, are much less dense and hard than typical metals such as iron, copper, and lead. On account of their relatively low ionization energies they form quite stable compounds which can be efficiently reduced to the metal only by their electrolysis in the molten state. It is noteworthy that calcium, strontium, and barium resemble each other more closely in their chemical properties than do beryllium and magnesium which differ from the other members of the group in several ways.

The elements of group IIA are known collectively as the *alkaline earth metals* or simply *alkaline earths*. The word earth, was applied in old days to a metallic oxide, and because the oxides of calcium, strontium, and barium produced alkaline solutions in water, these metals became known as the alkaline earth metals. This term is now commonly applied to all elements of group IIA.

## 1. Position of Group IIA Elements in the Periodic Table

The elements of group IIA have the elements of group IA, to their left and beryllium and magnesium have boron and aluminium respectively of group IIIA to their right. Compared to the preceding IA element, an element in group IIA has smaller atomic size, possesses higher ionization energy, and is less electropositive. On the other hand, an element in group IIA has larger atomic size and is more electropositive than the following element in group IIIA. These variations are reflected in the chemical properties of these groups. Thus, compared with boron, beryllium has a more metallic character, while non-metallic properties are less pronounced (in

| IA | IIA | IIIA |
|---|---|---|
| Li | Be | B |
| Na | Mg | Al |
| K | Ca | |
| Rb | Sr | |
| Cb | Ba | |
| Fr | Ra | |

accordance with the increased radius of the atom and smaller number of valency electrons). Similarly, magnesium is more metallic than aluminium, a fact reflected in the nature of the oxides—magnesium oxide, $MgO$, being a basic oxide while aluminium oxide, $Al_2O_3$, is an amphoteric oxide.

The important general features of the group IIA elements are reviewed below :

**1. Electronic configuration**. All group IIA elements have two *s*-electrons in their outer shell which is preceded by an 8-electron shell. Ignoring the filled inner shells, their electronic structures may be written $2s^2$, $3s^2$, $4s^2$, $5s^2$, $6s^2$, and $7s^2$. Owing to this similarity in electronic configuration, these elements form a well graded series of highly reactive, divalent metals.

**Table 9-1** *Electronic configuration of alkaline earth metals*

| Element | Symbol | At. No. | Electronic configuration | |
|---|---|---|---|---|
| Beryllium | Be | 4 | $1s^2; 2s^2$ | Or, [He] $2s^2$ |
| Magnesium | Mg | 12 | $1s^2; 2s^2, 2p^6; 3s^2$ | Or, [Ne] $3s^3$ |
| Calcium | Ca | 20 | $1s^2; 2s^2, 2p^4; 3s^2, 3p^6; 4s^2$ | Or, [Ar] $4s^2$ |
| Strontium | Sr | 38 | $1s^2; 2s^2, 2p^6; 3s^2, 3p^6, 3d^{10}; 4s^2, 4p^6; 5s^2$ | Or, [Kr] $5s^2$ |
| Barium | Ba | 56 | | [Xe] $6s^2$ |
| Radium | Ra | 88 | | [Rn] $7s^2$ |

**2. Valency and type of bonding**. In chemical combination, the alkaline earth metals lose their two electrons of the outer shell and form dipositive ions $M^{2+}$ (with the exception of beryllium). Hence, these elements are consistently divalent (valency $= +2$) and form ionic compounds.

The total energy required to produce gaseous divalent ions for group IIA elements (1st ionization energy + second ionization energy) is over four times as much as needed to ionize the group IA elements. However, the higher energy requirement is more than offset by the lattice energy* or the hydration energy** being proportionally greater. The compounds of the alkaline earth metals are therefore always divalent and ionic.

**3. Metallic character**. All the elements of group IIA are highly metallic with silvery lustre when pure. They are soft, malleable, and ductile though less so than the corresponding alkali metals. They are all good conductors of heat and electricity. Owing to their relatively low ionization energies, they are all strong reducing agents.

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*The lattice energy of a crystal is the energy evolved when one mole of the crystal is formed from its gaseous ions.

**The heat change, $\Delta H$, accompanying the hydration of one mole of ions.

4. **Flame tests.** The alkaline earth metals and their salts impart characteristic colours to the flame. In the flame, the electrons in their atoms absorb energy and are excited to higher energy levels. When an electron drops back to its original level, it gives out the extra energy which appears as visible light of a characteristic frequency causing the flame colouration (Ca brick red, Sr crimson, Ba apple green, Ra red).

5. **Chemical reactivity**. The ionization energies of the group IIA metals, while higher than those of the group IA elements, are still relatively low. As such, these elements are highly reactive, and readily react with oxygen, other non-metals, water, and acids.

*i. Action of air*. Like the alkali metals, the alkaline earth metals also oxidize quite rapidly in air and lose their lustre owing to the formation of oxide films.

*ii. Reaction with water*. All of these metals can displace hydrogen from water at ordinary temperatures. However, the reaction soon ceases with beryllium and magnesium since they become coated with the resulting hydroxides which are only sparingly soluble in water. The remaining four metals react vigorously with water evolving hydrogen and forming the hydroxides in solution.

$$M + 2H_2O \rightarrow M(OH)_2 + H_2\uparrow$$

*iii. Reaction with acids*. The alkaline earth metals stand high in the electrochemical series, and readily displace hydrogen from non-oxidizing acids. For example,

$$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2\uparrow$$

$$Ca + 2HCl \rightarrow CaCl_2 + H_2$$

As with other reactions, the vigour of the reaction increases from Be to Ra.

*iv. Combination with non-metals*. Group IIA elements combine readily with the halogens at appropriate temperatures forming halides $MX_2$ (M=an alkaline earth metal, X=a halogen). When heated they directly combine with hydrogen, oxygen, nitrogen, and carbon forming the hydrides $MH_2$, oxides MO, nitrides $M_3N_2$, and carbides $MC_2$ (containing $M^{2+}$ and $C{\equiv}C^{2-}$ ions) respectively.

6. **Compounds**. The compounds of the alkaline earth metals are always divalent and ionic. Since the divalent positive ions of these elements have an inert gas structure with no unpaired electrons, their compounds are diamagnetic and colourless, unless the anion is coloured. Most of the compounds are soluble in water. The sulphates of calcium, strontium, and barium are insoluble, and the carbonates, oxalates, chromates, and fluorides of the whole group are insoluble. This forms the basis of their separation and identification in qualitative analysis.

*i.* **Oxides and hydroxides**. The oxides of the alkaline earth metals of the general formula MO are formed by heating them in oxygen or by the thermal decomposition of their carbonates or nitrates.

$$2M + O_2 \rightarrow 2MO$$

$$MCO_3 \rightarrow MO + CO_2 \uparrow$$

$$2M(NO_3)_2 \rightarrow 2MO + 4NO_2 \uparrow + O_2 \uparrow$$

The oxides are all basic, except beryllium oxide which is amphoteric, and the basicity increases downward the group. Magnesium oxide reacts with water forming magnesium hydroxide, $Mg(OH)_2$ which is weakly basic. Calcium oxide reacts vigorously with water, and calcium hydroxide is a moderately strong base, while strontium and barium hydroxides are even stronger bases. The reason is that as the atom gets larger, the ionization energy decreases and the element becomes more basic.

*ii.* **Hydrides**. When heated in a current of hydrogen, the alkaline earth metals (except Be and Mg) form ionic hydrides, $MH_2$, which contain the ions $M^{2+}$ and $H^-$. These hydrides are good reducing agents, and react with water to form the metal hydroxides and hydrogen. For example,

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2 \uparrow$$

*iii.* **Carbonates and bicarbonates**. The carbonates of alkaline earth metals are precipitated on adding sodium or ammonium carbonate to solutions of their ions. All the carbonates are white solids which decompose on strong heating to give the metal oxide and carbon dioxide. The thermal stability of the carbonates increases from Be to Ba; the temperature of decomposition rising steadily from 100°C for $BeCO_3$ to 1360°C for $BaCO_3$.

The bicarbonates of alkaline earth metals are formed in solution when carbon dioxide is bubbled through the suspension of their carbonates in water. When the solution is boiled, the dissolved bicarbonate is decomposed to give back the carbonate which separates as a precipitate

$$MCO_3 + H_2O + CO_2 \underset{\text{heat}}{\rightleftharpoons} M(HCO_3)_2$$

Hence, it is not possible to isolate the bicarbonates in the solid state.

*iv. Halides*. Alkaline earth metals react with the halogens, directly and vigorously, to form their halides of the formula $MX_2$, where X is a halogen. Their halides can also be obtained by the action of halogen hydracids (HX) on the metals, their oxides, hydroxides, or carbonates :

$$M + X_2 \rightarrow MX_2$$

$$M + 2HX \rightarrow MX_2 + H_2 \uparrow$$

$$MCO_3 + 2HX \rightarrow MX_2 + H_2O + CO_2 \uparrow$$

Except beryllium halides, the halides of alkaline earth metals are all predominantly ionic. Except the fluorides, $MF_2$, the other metal halides are all soluble in water. They are usually hygroscopic and form hydrates, *e.g.*, $MgCl_2.6H_2O$, $CaCl_2.6H_2O$, $BaCl_2.2H_2O$, etc.

*v. Nitrates.* Nitrates of these metals can all be prepared by the reaction of nitric acid on the metals or on their oxides, hydroxides, and carbonates. They are obtained from solutions as hydrated salts. When heated, the nitrates are decomposed to yield the oxides. For example,

$$2Mg(NO_3)_2 \xrightarrow{\triangle} 2MgO + 4NO_2\uparrow + O_2\uparrow$$

$$2Ca(NO_3)_2 \xrightarrow{\triangle} 2CaO + 4NO_2\uparrow + O_2\uparrow$$

*vi. Sulphates.* Sulphates of alkaline earth metals, $MSO_4$, are formed by the action of sulphuric acid on metals, their oxides, hydroxides, carbonates, etc. The sulphates are stable to heat, and their solubility progressively decreases from $BeSO_4$ to $BaSO_4$.

*vii. Sulphides.* The sulphides of alkaline earth metals, $M_2S$, are not precipitated by hydrogen sulphide from the solutions of their salts as they are immediately hydrolysed to form soluble hydrosulphides, *e.g.*, $Ca(HS)_2$ :

$$2CaS + 2H_2O \longrightarrow Ca(HS)_2 + Ca(OH)_2$$

*viii. Carbides.* The alkaline earth metals form their carbides when their oxides are heated with carbon to high temperatures. They react with water or dilute acids and liberate hydrocarbons. Among the carbides, calcium carbide is the most important and is used for the preparation of acetylene. $C_2H_2$.

$$CaO + 3C \xrightarrow{1000°C} CaC_2 + CO\uparrow$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2\uparrow$$

7. **Gradation in properties**. The physical and chemical properties of the alkaline earth metals regularly vary as the atomic number increases. For example.

(1) Size of atoms and of ions regularly increases.

(2) The *metallic character and reactivity* increase. This is because the valency electrons are less strongly attracted to the nucleus and therefore more easily removed as the radius of the atom increases. The increase in the metallic character is seen in the *increase in the basic strength of hydroxides* from $Be(OH)_2$ to $Ra(OH)_2$. The increase in reactivity is reflected in reactions with non-metals. water and dilute acids. For example, beryllium hardly at all reacts with even steam, magnesium decomposes boiling water, while calcium, strontium, and barium decompose cold water with increasing vigour.

(3) The *electropositive character* and the strength as reducing agent increase.

(4) The *solubilities of hydroxides and fluorides* in water increase.

(5) The *thermal stability of carbonates* increases. The temperatures at which decomposition of the carbonates occurs are : $BeCO_3$ 100°C; $MgCO_3$ 540°C; $CaCO_3$ 900°C, $SrCO_3$ 1290°C; and $BaCO_3$ 1360°C.

(6) The *ionization energy, electronegativity,* and *hardness* decrease.

(7) *Solubilities of sulphates* and fluorides decrease.

## 2. Comparison of Elements of Groups IA and IIA

Alkaline earth metals differ from the corresponding alkali metals in having two valency electrons (alkali metals have one) and unit positive charge more on the nucleus. The extra charge on the nucleus draws the orbital electrons still inward. Hence, their atoms are smaller than the corresponding alkali metal atoms. Because removal of two orbital electrons further increases the effective nuclear charge, their ions are smaller than the corresponding alkali metalions. Thus, these elements are denser than group IA elements. Since these metals have two valency electrons which may take part in metallic bonding, the elements are harder than the alkali metals, and have much higher melting points. Since their atoms are smaller than those in group IA, the electrons are more tightly held and their first ionization potentials are higher than those of the alkali metals. Thus, their chemical properties are considerably modified. However, these two electrons are lost comparatively easily, leaving stable positively charged ions with inert gas structure like those of alkali metals. This accounts for the similarities in the properties of the elements of group IA and IIA.

**Table 8-2** *Comparison of the elements of groups IA and IIA*

| Property | Alkali metals | Alkaline earth metals |
|---|---|---|
| 1. Size of atoms and ions | Largest in the respective periods. | Largest, next to alkali metals. |
| 2. Hardness | Soft. | Moderately hard. |
| 3. M.P. | Low (28°—180°C). | Much higher (700°—1280°C). |
| 4. Electropositive nature | Highly electropositive and reactive. | Slightly less electropositive and less reactive. |
| 5. Valency | Consistency +1. | Consistently +2. |
| 6. With water and acids | React vigorously and displace hydrogen. | React less vigorously and displace hydrogen. |
| 7. Nature of compounds | Ionic, colourless (except when anion is coloured), soluble in water*. | Ionic, colourless, soluble in water except carbonates, phosphates, sulphates, and fluorides. |
| 8. Hydroxides | Very strongly basic; stable to heat*. | Less strongly basic; yield oxides on heating. |
| 9. Carbonates | Soluble, stable towards heat*. | Insoluble, decompose to oxides on strong heating. |

| | | |
|---|---|---|
| 10. Bicarbonates | Stable, solids at room temperature. | Exist only in solution. |
| 11. Action of heat on nitrates | Yield nitrites and oxygen. | Yield oxides, nitrogen dioxide, and oxygen. |
| 12. Hydrides | Ionic, contain $H^-$, form directly. | Ionic, contain $H^-$, form directly. |
| 13. Nitrides | Do not form directly*. | Form directly. |
| 14. Carbides | Do not form directly*. | Form directly. |
| 15. Flame test | Characteristic colorations. | Characteristic colorations. |

*Except lithium.

## MAGNESIUM, Mg

### 3. Magnesium in Nature

Magnesium ranks sixth in the order of abundance of elements in the earth's crust. However, it never occurs free in nature. The important minerals which contain magnesium compounds are :

(1) Magnesite, $MgCO_3$

(2) Dolomite, $MgCO_3.CaCO_3$

(3) Carnallite, $KCl.MgCl_2.6H_2O$

(4) Kainite, $K_2SO_4.MgSO_4.MgCl_2.6H_2O$

(5) Epsom salt, $MgSO_4.6H_2O$.

Sea water contains about 0·4 per cent magnesium as the chloride, sulphate, and bromide. Despite such a low proportion, sea water is the most important source of magnesium owing to its availability in virtually unlimited amount. Magnesium is an essential constituent of chlorophyll, a key substance in the photosynthesis reaction in green plants.

### 4. Extraction of Magnesium

**4-1. By electrolytic reduction of magnesium chloride.** Magnesium is extracted by the electrolysis of fused magnesium chloride. Sodium chloride is added to lower the temperature of fusion and to increase the electrical conductivity of the melt. The electrolysis is carried out in the reducing atmosphere of coal gas or hydrogen to protect the liberated magnesium, which is in the molten state, from reaction with atmospheric oxygen. The cell is externally heated to help the electrolyte molten at 700°C. The steel cell acts as the cathode while a graphite rod suspended vertically in the molten bath acts as the anode. The anode is surrounded by a porcelain tube with an exit for chlorine (Fig. 9-1). This arrangement prevents contact between the molten magnesium liberated at the cathode, which rises to the surface on account of its low density. It is periodically removed by ladles and is cast into ingots. The chlorine liberated at the anode is used to make more magnesium chloride from magnesium oxide.

A mixture of dehydrated carnallite, $KCl.MgCl_2.6H_2O$, and sodium chloride is often electrolysed to produce magnesium.

*Reactions* :

At anode : $Cl^- \rightarrow Cl + e^-$ ; $2Cl \rightarrow Cl_2\uparrow$

Al cathode : $Mg^{2+} + 2e^- \rightarrow Mg$

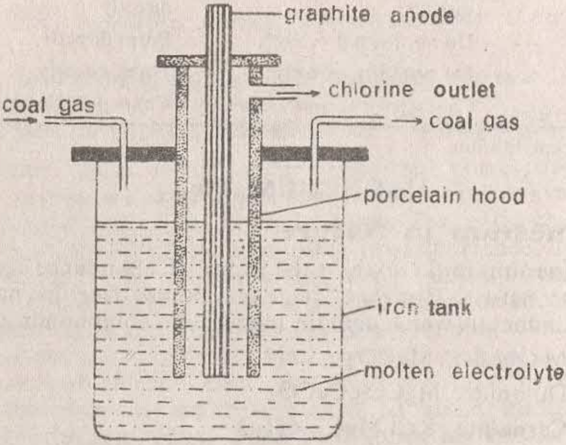

Fig. 9-1. Extraction of magnesium by the electrolysis of molten magnesium chloride.

**Production of anhydrous magnesium chloride.** Magnesium chloride is prepared mostly from sea water and to a small extent from the minerals magnesite and brucite.

(*a*) *From sea water.* Sea water contains $Mg^{2+}$ ions. It is treated with calcined dolomite* when the $Mg^{2+}$ ions are precipitated as magnesium hydroxide.

$$MgCl_2 + \underset{\text{calcined dolomite}}{(CaO.MgO)} + 2H_2O \rightarrow CaCl_2 + 2Mg(OH)_2$$

Magnesium hydroxide is filtered off and heated to obtain the oxide.

$$Mg(OH)_2 \xrightarrow{\triangle} MgO + H_2O\uparrow$$

Magnesium oxide is mixed with powdered coke and heated in an atmosphere of chlorine. Molten magnesium chloride is produced according to the reaction—

$$MgO + C + Cl_2 \xrightarrow{850°C} MgCl_2 + CO\uparrow$$

(*b*) *From magnesite* and *brucite*. The mineral magnsite $MgCO_3$, or brucite, $Mg(OH)_2$, is calcined to give magnesium oxide.

$$MgCO_3 \rightarrow MgO + CO_2\uparrow ; Mg(OH)_2 \rightarrow MgO + H_2O\uparrow$$

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*The mineral dolomite, $CaCO_3.MgCO_3$, upon calcination yields product consisting of CaO and MgO, called calcined dolomite.

$$CaCO_3.MgCO \xrightarrow{\text{calcine}} CaO.MgO + 2CO_2\uparrow$$

The magnesium oxide obtained is converted into magnesium chloride as before.

**4-2. By thermal reduction of magnesium oxide**. Magnesium is also prepared commercially by the reduction of magnesium oxide with ferrosilicon (an alloy of iron and silicon) at 1200—1250°C under reduced pressure (less than 4mm of mercury).

$$MgO + Fe \rightarrow FeO + Mg$$

$$2MgO + Si \rightarrow SiO_2 + 2Mg$$

The iron oxide and silica combine to form iron silicate slag, which is removed.

$$FeO + SiO_2 \rightarrow FeSiO_3 \textit{ (iron silicate slag)}$$

**4-3. Pure magnesium**. Pure magnesium of 99·999 per cent purity is obtained by repeated sublimation of commercial magnesium in vacuum.

## 5. Physical Properties of Magnesium

Magnesium is a silvery white, lustrous metal, density 1·74 g/cm³, m.p. 651°C, b.p. 1100°C. It is malleable and ductile at higher temperatures; it is softer and more plastic than beryllium. It is a good conductor of heat and electricity.

## 6. Reactions of Magnesium

Magnesium is a highly electropositive, reactive element, and shows great affinity for oxygen and other electronegative elements. Its important reactions are :

**1. With air**. Magnesium is rapidly dulled by oxidation by atmospheric oxygen. However, the oxide film protects the underlying metal from further action. When heated above its melting point in air, it burns with a brilliant white light, very rich in ultraviolet rays forming the oxide and the nitride.

$$2Mg + O_2 \rightarrow 2MgO \textit{ (magnesium oxide)}$$

$$3Mg + N_2 \rightarrow Mg_3N_2 \textit{ (magnesium nitride)}$$

**2. Combination with non-metals**. Besides oxygen and nitrogen, magnesium directly combines with phosphorus, sulphur, and the halogens at appropriate temperatures to form the corresponding binary compounds.

$$12Mg + 2P_4 \rightarrow 4Mg_3P_2 \text{ (magnesium phosphide)}$$

$$Mg + S \rightarrow MgS \quad \text{(magnesium sulphide)}$$

$$Mg + X_2 \rightarrow MgX_2 \quad \text{(magnesium halide)}$$

**3. With water**. Magnesium reacts very slowly with cold water since the resulting hydroxide, $Mg(OH)_2$, is only slightly soluble. It decomposes boiling water slowly, but rapidly displaces hydrogen from steam.

$$Mg + H_2O \rightarrow MgO + H_2\uparrow$$

4. **With acids.** Magnesium comes before hydrogen in the electrochemical series. Therefore, it readily displaces hydrogen from acids, including carbonic acid, $H_2CO_3$.

$$Mg + 2H^+ \rightarrow Mg^{2+} + H_2 \uparrow$$

$$Mg + 2H_2CO_3 \rightarrow Mg(HCO_3)_2 + H_2 \uparrow$$

It is also attacked by alkali hydrogen carbonates and various salts which give acid reaction by hydrolysis.

5. **As a reducing agent.** Magnesium is a powerful reducing agent. It continues to burn in carbon dioxide and reduces it to carbon.

$$2Mg + CO_2 \rightarrow 2MgO + C$$

It reduces the halides of titanium, uranium, etc. on heating.

$$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$$

$$UF_4 + 2Mg \rightarrow U + 2MgF_2$$

The great reducing tower of magnesium is utilized in separating many metals and non-metals, such as titanium, zirconium, boron, silicon, etc. from their halides and oxides.

## 7. Uses of Magnesium

1. Most of the production of magnesium is used in making alloys, the most important of which are those with aluminium and zinc. These light-weight alloys offer a combination of lightness and strength. Hence, these are used extensively in building aeroplanes, guided missiles, speed boats, dirigibles, racing cars, ladders, light-weight garden furniture, etc. Important alloys are the '*electrons*' (3-10% Al, 0·2-3% Zn, and the rest Mg), and *magnalium* (5-30% Mg, rest Al). These alloys are not only light but are also much stronger than the individual metals of which they are composed.

2. Mixtures of powdered magnesium and oxidizing agents are used in photographic flashlight powders, signal flares, fireworks, and incendiary bombs.

3. Magnesium is used as a reducing agent in the extraction of titanium, vanadium, uranium, zirconium, and other metals.

4. It is also used as a deoxidizer in metallurgy to remove oxygen dissolved in molten metals.

5. Lumps of magnesium are attached to pipelines, underground storage tanks, hulls of ships, etc. to protect copper or iron against corrosion; the more reactive magnesium corrodes in preference to steel or copper. This kind of protection is known as *sacrificial corrosion*.

## COMPOUNDS OF MAGNESIUM

### 8. Magnesium Oxide, MgO

It is usually prepared by calcining the mineral magnesite, $MgCO_3$. It is a white loose powder, commonly known as magnesia. Owing to its high melting point (above 3000°C), it is used as a refractory* for making crucibles, pipes, and bricks.

### 9. Magnesium Hydroxide, $Mg(OH)_2$

Magnesium oxide slowly combines with water to form magnesium hydroxide. It is precipitated as a sludge on adding an alkali to a solution of $Mg^{2+}$ ions.

$$Mg^{2+} + 2\,OH^- \rightarrow Mg(OH)_2$$

A suspension of magnesium hydroxide in water, called *milk of magnesia*, is used as a mild laxative and as an antacid to neutralize excess stomach acid.

### 10. Magnesium Nitride, $Mg_3N_2$

*Preparation.* It is made by heating magnesium strongly in nitrogen or ammonia.

$$3Mg + N_2 \rightarrow Mg_3N_2$$

$$3Mg + 2NH_3 \rightarrow Mg_3N_2 + 3H_2$$

*Properties.* It is a colourless solid. It reacts with water, even in cold, giving ammonia.

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3\uparrow$$

### 11. Magnesium Chloride, $MgCl_2$

Magnesium chloride occurs naturally in sea water and in the mineral carnallite, $KCl.MgCl_2.6H_2O$.

*Preparation.* It can be prepared by dissolving magnesium metal, magnesium oxide, or magnesium carbonate in dilute hydrochloric acid. On concentrating the resulting solution $MgCl_2.6H_2O$ crystallises out.

*Properties.* Hydrated magnesium chloride is a colourless, crystalline, deliquescent solid, highly soluble in water. When heated, it first loses four molecules of water of hydration and then undergoes partial hydrolysis without yielding the anhydrous salt.

$$MgCl_2 + H_2O \rightleftharpoons Mg(OH)Cl + HCl$$

**Anhydrous magnesium chloride** is prepared—

1. By heating the hydrate $MgCl_2.6H_2O$ in a current of dry chlorine. This shifts the equilibrium in the above reaction to the left.

---

*Refractory is any material which is not damaged by heating to high temperatures.

2. By heating the double salt of magnesium chloride and ammonium chloride obtained by evaporating a solution containing equimolecular quantities of the two salts.

$$MgCl_2.NH_4Cl.6H_2O \rightarrow MgCl_2.NH_4Cl + 6H_2O\uparrow$$

$$MgCl_2.NH_4Cl \rightarrow MgCl_2 + NH_3\uparrow + HCl\uparrow$$

The dissociation of ammonium chloride ($NH_4Cl \rightarrow NH_3 + HCl$) provides an atmosphere of HCl.

3. By heating magnesium oxide strongly with carbon and chlorine.

$$MgO + C + Cl_2 \rightarrow MgCl_2 + CO\uparrow$$

*Uses.* (1) In the electrolytic extraction of magnesium. (2) In cotton dressing. (3) In making *Sorel's cement*, which is used for dental stopping and for cementing glass with metals. It is made by mixing a saturated solution of magnesium chloride with magnesium oxide. The resulting paste sets to a hard marble like mass of the composition. $MgCl_2 5MgO.xH_2O$.

## 12. Magnesium Carbonate, $MgCO_3$

*Preparation.* It occurs naturally as magnesite and dolomite. It is made by adding sodium hydrogen carbonate solution to the solution of a magnesium salt.

$$\underset{\text{(in magnesium salt)}}{Mg^{2+}} + 2NaHCO_3 \rightarrow MgCO_3\downarrow + 2Na^+ + H_2O + CO_2\uparrow$$

*Properties.* It is a white solid, almost insoluble in water but readily soluble in acids forming corresponding magnesium salts with the liberation of carbon dioxide.

$$MgCO_3 + 2HCl \rightarrow MgCl_2 + H_2O + CO_2\uparrow$$

It also dissolves in water containing dissolved carbon dioxide forming magnesium hydrogen carbonate.

$$MgCO_3 + H_2O + CO_2 \leftrightarrows Mg(HCO_3)_2$$

On heating, it decomposes to give magnesium oxide and carbon dioxide

$$MgCO_3 \xrightarrow{\triangle} MgO + CO_2$$

*Uses.* (1) It is used in toothpastes, and as a filler for paper, rubber, and paints. (2) In the mineral form it is used as a source of magnesium and many of its compounds.

## 13. Magnesium Sulphate, $MgSO_4$

*Preparation.* It occurs naturally as kieserite and is present in sea water and in some springs. It is made commercially by fractional crystallization from minerals or by the action of dilute sulphuric acid on magnesium carbonate

$$MgCO_3 + H_2SO_4 \rightarrow MgSO_4 + H_2O + CO_2\uparrow$$

Crystallization at room temperature yields the heptahydrate, $MgSO_4.7H_2O$, called the Epsom salt. On heating to 200°C, it gives anhydrous magnesium sulphate.

*Uses*. (1) As a laxative. (2) As a filler for paper. (3) In the treatment of textile fibres to render them non-inflammable. (4) In the dyeing and tanning processes.

## 14. Interconversion of Compounds

A given soluble compound of magnesium can be converted into another soluble compound through the preparation of magnesium carbonate by adding sodium hydrogen carbonate to the solution of the given compound. Magnesium carbonate is filler off and treated with the appropriate acid to obtain the desired compound. For example,

$$MgSO_4 \xrightarrow{NaHCO_3} Mg(OH)_2 \downarrow \xrightarrow{HCl} MgCl_2$$

$$MgCl_2 \xrightarrow{NaHCO_3} Mg(OH)_2 \downarrow \xrightarrow{H_2SO_4} MgSO_4$$

An insoluble compound such as magnesium oxide, magnesium carbonate, or magnesium sulphide can be converted into a soluble compound by treatment with an appropriate acid. For example,

$$Mg(NO_3)_2 \xleftarrow{HNO_3} MgCO_3 \xrightarrow{HCl} MgCl_2$$

### CALCIUM, Ca

## 15. Calcium in Nature

Calcium is too reactive to occur free in nature. In the combined state it is widely distributed and occurs in various minerals as—

(*i*) *Carbonate* in limestone, marble, chalk, marine shells, pearls, etc. Dolomite is a double carbonate of calcium and magnesium, $CaCO_3.MgCO_3$.

(*ii*) *Sulphate* in anhydrite, $CaSO_4$, and gypsum, $CaSO_4.2H_2O$.

(*iii*) *Fluoride* in fluorspar, $CaF_2$, and fluorapatite, $3Ca_3(PO_4)_2.CaF_2$.

(*iv*) *Phosphate* in phosphorite, $Ca_3(PO_4)_2$.

Soluble salts of calcium are present in ground waters and sea water. Shells of marine animals are made of mainly calcium carbonate while bones and teeth of animals are largely made of calcium phosphate.

Calcium is one of the basic elements of human life, an intake of approximately 1 gram of calcium ion being needed every day.

## 16. Extraction of Calcium

Calcium is extracted by the electrolysis of fused anhydrous calcium chloride to six parts of which is added 1 part of calcium fluoride. This mixture melts at 644°, about 130° lower than calcium chloride alone. The electrolysis is carried out in a furnace lined with graphite, which serves as the anode. The cathode is a steel pipe which can be moved upward as well as downward. The cell and the cathode are both water-cooled (Fig. 9-2).

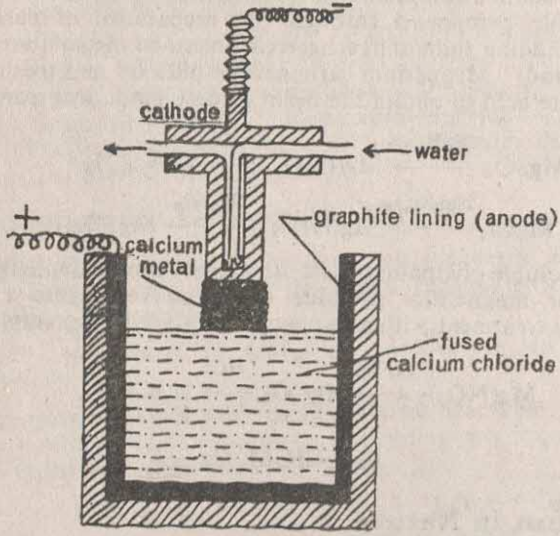


Fig. 9-2. Electrolytic production of calcium.

The water-cooled cathode is so adjusted that its tip is just below the surface of the electrolyte. As the metal deposits in the molten state, the cathode is slowly raised. The molten calcium adheres to the cathode and solidifies as it rises up with it. Thus, an irregular rod of calcium is formed. Subsequently, the lower end of this rod begins to serve as the cathode. During its upward movement, the rod of calcium is protected from oxidation by a layer of solidified electrolyte. When the cathode has reached its upper extreme, the rod of calcium is removed. It contains about 85 per cent calcium; the rest being the solidified electrolyte. The rods are melted and cast in an atmoshere of argon or distilled under high vacuum to obtain pure calcium.

## 17. Physical Properties and Reactions of Calcium

(*i*) Calcium is a silver-white, light metal (sp. gr. = 1·55). It is malleable and ductile.

(*ii*) *Action of air*. In the air, it becomes coated with a layer of oxide, hydroxide, and carbonate. When gently heated in air, it burns with a bright reddish flame, forming the oxide $CaO$. A little nitride, $Ca_3N_2$, is also formed simultaneously.

(*iii*) *Action of water*. Calcium reacts with water to form its hydroxide and liberate hydrogen.

$$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2 \uparrow$$

(*iv*) *Action of acids*. Calcium reacts vigorously with acids to form calcium salts and liberate hydrogen.

(*v*) *Combination with non-metals*. Calcium is a very reactive metal. Besides oxygen and nitrogen, it combines directly when heated with hydrogen, sulphur, halogens, and phosphorus forming the hydride ($CaH_2$), sulphide ($CaS$), halides ($CaX_2$; $X = Cl, Br, I$), and the phosphate ($Ca_3P_2$) respectively.

## 18. Uses of Calcium

(*i*) *As a dehydrating agent* for drying alcohol, etc.

(*ii*) *As a deoxidizing agent* for such metals as copper, magnesium, aluminium, etc., and for absorbing air from castings.

(*iii*) *As a hardening agent* for lead used in making bearings, covering cables, etc.

(*iv*) *As a reducing agent* in the production of certain metals from their oxides.

(*v*) *For the manufacture of calcium hydride* (*hydrolith*).

## COMPOUNDS OF CALCIUM

## 19. Calcium Hydride, Hydrolith, $CaH_2$

*Preparation*. It is prepared by passing hydrogen over heated calcium.

$$Ca + H_2 \rightarrow CaH_2$$

*Properties*. (1) It is a colourless, ionic solid. It yields hydrogen on the anode when electrolysed in the fused state.

(2) If reacts with water liberating hydrogen.

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2 \uparrow$$

(3) It absorbs carbon dioxide forming calcium formate.

$$CaH_2 + 2CO_2 \rightarrow (H.COO)_2Ca$$

*Use*. As a convenient source of hydrogen for baloons, etc. under the trade name 'hydrolith'.

## 20. Calcium Oxide Quicklime, $CaO$

*Preparation*. It is made industrially by heating limestone in kilns to 800–1000°C by means of producer gas.

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow$$

*Properties.* (1) It is a white amorphous powder, m.p. 2600°C, which becomes incandescent on heating and emits intensely bright light (called *limelight*).

(2) It vigorously combines with water forming *shaked lime* or calcium hydroxide.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

(3) It is a strongly basic oxide and reacts with acids and acidic oxides, *e.g.*, $SiO_2$, forming salts. For example,

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$

$$CaO + SiO_2 \xrightarrow{\Delta} CaSiO_3 \text{ (calcium silicate)}$$

(4) It reacts with chlorine in two different ways : when moist, it gives bleaching powder; at red heat, it forms calcium chloride with the liberation of oxygen.

$$CaO + Cl_2 \xrightarrow{\text{moisture}} CaOCl_2 \text{ (bleaching powder)}$$

$$2CaO + 2Cl_2 \xrightarrow{\text{red heat}} 2CaCl_2 + O_2 \uparrow$$

(5) Slaked lime reacts with ammonium salts upon heating, liberating ammonia

$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O + 2NH_3 \uparrow$$

(6) When heated to 2000°C with carbon, it gives calcium carbide, $CaC_2$.

$$CaO + 3C \rightarrow CaC_2 + CO \uparrow$$

*Uses.* (1) For making *mortar*, which is a paste-like mixture of one part of slaked lime, three or four parts of sand, and enough water. It is used in the building industry for binding bricks and for plastering and is an economic substitute for cement.

(2) In the manufacture of calcium carbide, $CaC_2$, and bleaching powder, CaCl(OCl).

(3) As *milk of lime* for the purification of sugar and for white washing. (The milky suspension of calcium oxide in water is called milk of lime).

(4) In the laboratory as a drying agent and for making soda-lime and lime water.

## 21. Calcium Carbide, $CaC_2$

*Preparation.* It is made by heating quicklime with powdered coke to 2000°C in an electric furnace.

$$CaO + 3C \rightarrow CaC_2 + CO \uparrow$$

The charge is heated by the heat of the electric are struck between the graphite electrode suspended vertically and another graphite electrode at the bottom. The resulting molten calcium carbide is run off periodically, cooled, and broken into lumps.

*Properties.* (*i*) It is a hard, crystalline substance which is white when pure. The commercial product is usually dark grey due to impurities.

(*ii*) It reacts readily with cold water producing acetylene.

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2 \uparrow$$

(*iii*) When heated to 1000–1100°C in nitrogen, in forms calcium cyanamide, $CaCN_2$, and free carbon.

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

*Uses.* (1) As a source of acetylene which is used as a fuel in welding and metal cutting, and as a raw material for the production of a large number of organic compounds and synthetic rubber.

(2) In the manufacture of calcium cyanamide, which is used as a fertilizer.

## 22. Calcium Carbonate, $CaCO_3$

*Preparation.* This substance occurs in nature in many forms, *e.g.*, marble, chalk, limestone, etc. It is formed as a fine precipitate when carbon dioxide is passed through lime water or when a soluble carbonate is added to the solution of a calcium salt.

$$\underset{\text{lime water}}{Ca(OH)_2} + CO_2 \longrightarrow CaCO_3 \downarrow + H_2O$$

$$\underset{\text{in calcium salt}}{Ca^{2+}} + \underset{\text{soluble carbonate}}{CO_3{}^{2-}} \longrightarrow CaCO_3 \downarrow$$

*Properties.* Calcium carbonate is a white solid, almost insoluble in water. It dissolves in water containing dissolved carbon dioxide forming calcium hydrogen carbonate, and in acids forming corresponding calcium salts with the liberation of carbon dioxide.

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$$

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2 \uparrow$$

On strong heating, calcium carbonate decomposes to yield calcium oxide and carbon dioxide.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \uparrow$$

*Uses.* Different forms of calcium carbonate are used for different purposes : (*i*) *Limestone* is used for the manufacture of lime, cement, washing soda, glass, and as a flux in metallurgy. (*ii*) *Marble* is used in the construction of buildings and in the laboratory for producing carbon dioxide. (*iii*) *Chalk* (mineral) is used as a filler in paints. (*iv*) *Precipitated chalk* (calcium carbonate) is used in toothpastes, etc.

## 23. Calcium Chloride, $CaCl_2$

*Preparation.* It is present in sea-water and ground water. It is obtained as a by-product in the manufacture of sodium carbonate by the Solvay process. It may be prepared by the action of hydrochloric acid on calcium carbonate.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2 \uparrow$$

The solution on evaporation deposits hydrated calcium chloride, $CaCl_2 \cdot 6H_2O$.

*Properties.* Calcium chloride in a white, very deliquescent substance. It is highly soluble in water, 159 g of the salt dissolves in 100 g of water at the boiling point. When strongly heated, it loses all water of hydration yielding the anhydrous salt.

Anhydrous calcium chloride readily absorbs water to form $CaCl_2\ 6H_2O$. It also absorbs ammonia to form $CaCl_2\ 8NH_3$.

*Uses.* (*i*) Fused calcium chloride is used as a dessicating agent for drying gases and liquids.

(*ii*) It is sprinkled on roads where it absorbs moisture, becomes moist, and keeps the dust down.

(*iii*) It is mixed with ice to produce freezing mixtures with temperatures as low as —55°C.

(*iv*) Calcium chloride is used for the production of calcium by its electrolysis in the fused state.

## 24. Calcium Sulphate, $CaSO_4$

This compound occurs in nature as anhydrite, $CaSO_4$, and gypsum, $CaSO_4.2H_2O$. In the laboratory, it may be prepared by adding dilute sulphuric acid or any soluble sulphate (which give $SO_4^{2-}$ ions) to an aqueous solution of a calcium salt (which contains $Ca^{2+}$ ions).

$$CaCl_2 + H_2SO_4 \rightarrow CaSO_4 \downarrow + 2HCl$$
$$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4 \downarrow$$

Calcium sulphate thus obtained is in the form of the dihydrate, $CaSO_4 \cdot 2H_2O$.

*Gypsum*, *i.e.*, calcium sulphate dihydrate, when heated to 120°C loses three-quarters of its water of crystallization to form the hemihydrate, $CaSO_4.\frac{1}{2}H_2O$ or $2CaSO_4.H_2O$, called **plaster of Paris**. A paste of plaster of Paris with water sets to a hard mass with the composition of $CaSO_4.2H_2O$. This change is accompanied by a slight expansion.

If gypsum is heated above 200°C, whole of its water of crystallization is lost and the anhydrous calcium sulphate is produced. The mass now obtained does not set with water and is called *dead burnt gypsum*.

*Uses*. (*i*) Calcium sulphate (gypsum) is used for making plaster of Paris. Plaster of Paris is used for the making of moulds, etc., in surgery for plastering fractured bones, and for making 'chalk' sticks for writing on black boards.

(*ii*) Gypsum is used in the manufacture of cement, in agriculture to correct the alkalinity of soils, and for impregnating filter papers.

(*iii*) Anhydrous calcium sulphate is used as a drying agent for gases and organic liquids.

## 25. Calcium Nitrate, $Ca(NC_3)_2$

It occurs in the soil and is used by the plants. It is made on a large scale by the action of dilute nitric acid upon limestone. On evaporating the solution, colourless, deliquescent crystals of calcium nitrate separate.

$$\underset{\text{limestone}}{CaCO_3} + 2HNO_3 \rightarrow \underset{\text{calcium nitrate}}{Ca(NO_3)_2} + H_2O + CO_2\uparrow$$

On heating, it decomposes to give calcium oxide, nitrogen dioxide, and oxygen.

$$2Ca(NO_3)_2 \xrightarrow{\Delta} 2CaO + 4NO_2\uparrow + O_2\uparrow$$

A mixture of calcium nitrate and calcium oxide is used in agriculture as a fertilizer under the name *Norwegian saltpeter*.

## 26. Superphosphate of Lime

*Preparation*. This important phosphatic fertilizer is made by treating calcium phosphate (phosphorite rock or bone ash) with a calculated quantity of sulphuric acid, usually chamber acid.

$$\underset{\substack{\text{calcium}\\ \text{phosphate}}}{Ca_3(PO_4)_2} + 2H_2SO_4 + 5H_2 \rightarrow \underset{\substack{\text{calcium dihydrogen}\\ \text{phosphate}}}{Ca(H_2PO_4)_2H_2O} + \underset{\text{gypsum}}{2[CaSO_4.2H_2O]}$$

The resulting mixture of monocalcium phosphate and gypsum solidifies to a hard mass. It is finely ground and sold under the name superphosphate of lime. It usually contains a little undecomposed calcium phosphate.

*Properties*. Superphosphate of lime is a white substance, much more soluble than normal calcium phosphate.

*Use*. It is used as a phosphatic fertilizer. It easily dissolves in soil moisture and becomes available for assimilation by plants.

## 27. Bleaching Powder

Bleaching powder is a handy source of chlorine which, being solid, is more convenient and safer to transport than gaseous or liquid chlorine.

**27-1. Preparation**. Bleaching powder is made by the interaction of slaked lime (calcium hydroxide) and chlorine in towers so designed that the finely powdered slaked lime passes downward against a stream of the upflowing chlorine (*counter current principle*). The reaction is exothermic, and the rate of interaction is so controlled that the temperature does not go above 35°C to prevent the formation of calcium chlorate. The product is a white, amorphous solid, whose actual composition is not known. However, it behaves chemically as if it were a mixture of calcium hypochlorite, $Ca(ClO)_2$, and basic calcium chloride, $CaCl_2.Ca(OH)_2.H_2O$. It is usually shown in chemical formula as calcium chloride hyprochlorite. $CaCl(OCl)$.

**27-2. Properties and reactions.** (1) Bleaching powder is a pale-white amorphous powder with a strong odour of chlorine. It is soluble in water, and the solution gives the tests for $Ca^{2+}$, $Cl^-$, and $ClO^-$ ions. The insoluble residue left when bleaching powder is added to water consists of unchanged lime.

(2) *Reaction with dilute acids.* When bleaching powder is treated with an insufficient quantity of a dilute acid, hypochlorous acid is formed.

$$CaCl(OCl) + HCl \rightarrow CaCl_2 + HClO$$

With excess of the dilute acid, however, chlorine is liberated.

$$CaCl(OCl) + 2HCl \rightarrow CaCl_2 + H_2O + Cl_2 \uparrow$$

$$CaCl(OCl) + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2 \uparrow$$

The amount of chlorine thus liberated is called its '*available chlorine*'. It is a measure of the quality of the bleaching powder. A freshly made sample contains about 36 per cent of available chlorine.

In moist air, bleaching powder, gradually loses its chlorine by the combined action of water (moisture) and carbon dioxide, and its market value goes down.

$$CaCl(OCl) + H_2O + CO_2 \rightarrow CaCO_3 + H_2O + Cl_2 \uparrow$$

(3) *Oxidizing reactions.* Like sodium hypochlorite, bleaching powder also contains the hypochlorite ion, $ClO^-$, and gives similar oxidizing reactions. It liberates iodine from acidified solutions of iodides, and oxidizes manganese (II) salts to manganese dioxide and lead (II) salts to lead dioxide in the presence of alkalis.

(4) *Decomposition.* When a thin paste of bleaching powder is heated in the presence of a little cobalt chloride, it is catalytically decomposed with evolution of oxygen.

$$2CaCl(OCl) \rightarrow 2CaCl_2 + O_2 \uparrow$$

**27-3. Uses.** (1) *As a bleaching agent.* Bleaching powder is the cheapest bleaching material available, and is extensively used for bleaching raw cotton, linen, and wood pulp for paper making.

(2) *As a disinfectant* (under the name 'chloride of lime').

(3) *In the manufacture of chloroform* for the oxidation of ethyl alcohol and the chlorination of the resulting acetaldehyde.

(4) *As an oxidizing agent* in certain chemical industries.

## 28. Mortar and Cement

**28-1. Mortar.** A paste-like mixture of one part of slaked lime, three or four parts of sand, and enough water is called *mortar*. It is used for binding bricks and for plastering. On standing in air it sets to a hard mass due to the loss of moisture by evaporation and the conversion of slaked lime into crystalline calcium carbonate by the action of atmospheric carbon dioxide.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

The calcium carbonate binds together the particles of sand and unchanged lime. The sand renders the mass porous and prevents the mortar from craking as it sets.

**28-2. Portland cement.** Portland cement, often called simply cement, is one of the most important building materials. It is essentially a finely powdered mixture of various silicates, aluminates, and aluminoferrites of calcium, formed form limestone and clay.

*Manufacture*. Powdered limestone (which provides lime) and clay (which provides silica and alumina) are thoroughly mixed in proper proportions, dry or wet. *Dry process* is employed in the case of hard limestone while the *wet process* is suitable when the raw materials are soft, fuel is cheap, and the climate is fairly moist. The dry mixture or the wet 'slurry' is roasted at about 1500°C in a cylindrical rotary kiln until it sinters. The kiln consists of a large steel tube, slightly inclined and lined on the inside with firebricks. The cement mixture is fed at the raised end, while a blast of burning coal dust, oil, or gas is blown in from the other end. Due to the incline and slow rotatory motion of the kiln, the mixture slowly slides downward into zones of increasing heat. In the central part, where the temperature is 800 – 1000°C, the limestone decomposes to give lime.

$$CaCO_3 \rightarrow CaO + CO_2$$

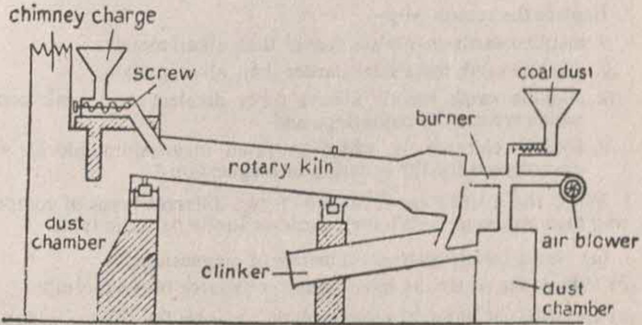


Fig. 2-3. Rotary kiln for the manufacture of cement.

In the lower part, the temperature is 1400 - 1600°. Here lime reacts with the silica and alumina in clay to produce a mixture of calcium silicate and aluminate in the form of greenish-black hard balls about the size of pea, *called clinker*. The clinker is allowed to cool and then ground with 2-3 per cent of gypsum, $CaSO_4.2H_2O$, to an exceedingly fine powder. Addition of gypsum retards the setting of the cement. The dirty greenish, heavy powder thus obtained is the Portland cement.

In use, cement is mixed with sand and enough water to give the mixture the consistency of paste. On standing, this paste undergoes complex chemical changes and sets to a hard rock-like mass. It is widely used in the construction of buildings, roads, etc. Its inertness toward water makes it indispensable for the construction of dams and submarine structures. The *concrete* used for the construction of roads, foundations, floors, etc. is made by adding water to a mixture of cement, gravel or crushed rock, and sand. It may also be poured into moulds in which it sets to a hard rock-like mass. Structures made of concrete in which steel rods or netting is embedded are called *reinforced concrete* structures. These structures possess great strength and are used in the construction of bridges, roofs, tanks, etc.

## 29. Interconversion of Compounds

The interconversion of soluble compounds of calcium can be achieved through the precipitation of insoluble calcium carbonate and the treatment of the latter by an appropriate reagent. For example,

$$CaCl_2 \xrightarrow{Na_2CO_3} CaCO_3\downarrow \xrightarrow{HNO_3} Ca(NO_3)_2$$

$$Ca(NO_3)_2 \xrightarrow{Na_2CO_3} CaCO_3\downarrow \xrightarrow{2HCl} CaCl_2$$

### Questions

1. Arrange the hydroxides of the alkaline earth metals in the order of increasing basicity, and explain the reason for variation.

2. Explain the reason why—

*i.* alkaline earth metals are denser than alkali metals,

*ii.* alkaline earth metals are harder than alkali metals,

*iii.* alkaline earth metals always form divalent and ionic compounds which are usually colourless, and

*iv.* sodium chloride is added to fused magnesium chloride when it is electrolysed for the isolation of magnesium ?

3. Write the names or formulae of two different types of compounds of calcium and magnesium to justify their position in the periodic table.

4. (*a*) Name three important minerals of magnesium ?

(*b*) Why is sea water the most important source of magnesium ?

(*c*) Describe in brief the electrolytic process for the extraction of magnesium. Give equations for the electrode reactions that occur.

(*d*) Give the names of two alloys of magnesium and their approximate compositions. What are these alloys used for ? What properties of these alloy make them useful for these applications ?

5. (*a*) Give two reactions for the preparation of anhydrous magnesium chloride. Why cannot anhydrous magnesium chloride be prepared by heating the hydrated chloride ? List its important uses.

(*b*) Describe the preparation, properties, and uses of magnesium carbonate.

6. (*a*) Give a brief account of the manufacture of calcium. Mention two compounds of calcium which occur widely in nature.

(*b*) Compare the action of calcium and sodium with cold water.

(*c*) How will you prepare samples of the following from calcium carbonate: bleaching powder and calcium sulphate ?

[**Hint**. Calcium carbonate will be converted into calcium oxide by strong heating. Calcium oxide will be slaked with water to obtain calcium hydroxide, $Ca(OH)_2$. Calcium hydroxide will be converted into bleaching powder by interaction with chlorine and into calcium sulphate by neutralizing it with sulphuric acid.]

7. (*a*) How is calcium oxide made industrially ?

(*b*) Describe the important properties of calcium oxide.

(*c*) List the important uses of calcium oxide.

8. Give the preparation, properties, and uses of—

*i*. calcium carbide,

*ii*. calcium sulphate, and

*iii*. superphosphate of lime.

9. Write explanatory notes on mortar and Portland cement.

10. What happens when—

*i*. Hydrated magnesium chloride is heated,

*ii*. magnesium oxide mixed with coke is heated in a current of dry chlorine,

*iii*. magnesium nitride reacts with water,

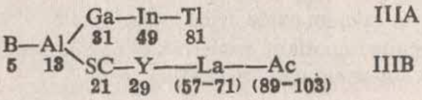
*iv*. bleaching powder is treated with excess of dilute sulphuric acid, and

*v*. bleaching powder is exposed to moist air ?

# 10

# Elements of Group IIIA

Group III of the periodic table contains as many as 37 elements arranged in the sub-groups A and B.



This large number of elements is due to the presence of two series of transition elements in this group : the *lanthanide series* or the cerium family (elements 57-71) and the *actinide series* or the thorium family, (element 89−103) both in the subgroup B.

Boron and aluminium are the typical elements of group III, but they are more closely related to the members of the sub-group IIIA in valency and chemical behaviour. Many chemists do not favour the inclusion of boron and aluminium in either subgroup, and prefer to consider them a family by themselves.

## 1. Position of Group IIIA Elements in Periodic Table

**1. Electronic configuration.** The elements of group IIIA have three valence electrons, and are distinguished by the $ns^2\ np^1$ ending in their electronic configurations. Thus, they belong to the $p$-block of elements.

**Table 10-1.** *Electronic configurations of group IIIA elements*

| Element | Symbol | At. No. | Electronic configuration | |
|---|---|---|---|---|
| 1. Boron | B | 5 | $1s^2; 2s^2, 2p^1$ | Or, [He] $2s^2, 2p^1$ |
| 2. Aluminium | Al | 13 | $1s^2; 2s^2, 2p^6; 3s^2\ 3p^1$ | Or, [Ne] $3s^2, 3p^1$ |
| 3. Gallium | Ga | 31 | $1s^2; 2s^2, 2p^6; 3s^2, 3p^6, 3d^{10}; 4s^2, 4p^1$ | Or, [Ar] $4s^2, 4p^1$ |
| 4. Indium | In | 49 | | [Kr] $5s^2, 5p^1$ |
| 5. Thallium | Tl | 81 | | [Xe] $6s^2, 6p^1$ |

**2. Valency.** All of the Group IIIA elements show a valency of +3. In addition to the +3 valency, gallium, indium, and thallium also show +1 valency in many compounds. The +3 valency is in fact common to the elements of both the subgroups IIIA and IIIB. This will be clear from the formulae of some of the compounds of aluminium and cerium, *e.g*, $Al_2O_3$, $Ce_2O_3$; $Al(OH)_3$, $Ce(OH)_3$; $Al_2(SO_4)_3$, $Ce_2(SO_4)_3$; etc.

3. **Type of bonding.** Owing to the small size of their ions which carry high electrical charge and the large values for the sum of the first three ionization energies, the elements tend to form covalent bonds. However, with the exception of boron which is always covalent, they can all exist in aqueous solutions as hydrated positive trivalent ions, *e g.*, $Al^{3+}$, $Ga^{3+}$, etc. This is possible because of the large amount of hydration energy evolved which compensates the high ionization energy.

4. **Metallic character.** The Group IIIA elements vary from nonmetallic for boron to metallic for the others. However, the metallic properties of these elements are much less pronounced than in the corresponding elements of the Groups IA and IIA. The first element boron, having a very small atom, exhibits markedly non-metallic properties. In fact, boron resembles silicon and carbon, the nonmetals of group IVA, more than it does the other Group IIIA elements. It is brittle and is not a good conductor of heat or electricity.

5. **Chemical reactivity.** Group IIIA elements are chemically far less reactive than the elements of Groups IIA and IA. They are practically unaffected by air and water. However, boron and aluminium react rather vigorously with most electronegative elements, such as nitrogen, oxygen, and halogens, at higher temperatures.

6. **Reaction with alkalis.** Boron and aluminium react with alkalis to form borates and aluminates respectively, and liberate hydrogen.

$$2B + 2NaOH + 2H_2O \rightarrow \underset{\text{sodium metaborate}}{2NaBO_2} + 3H_2\uparrow$$

$$2Al + 2NaOH + 2H_2O \rightarrow \underset{\text{sodium metaaluminate}}{2NaAlO_2} + 3H_2\uparrow$$

7. **Reducing action.** Both boron and aluminium are powerful reducing agents at high temperatures.

$$4B + 3CO_2 \rightarrow 2B_2O_3 + 3C$$

$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$$

8. **Compounds.** The compounds of these elements are predominantly covalent, with the possible exception of $AlF_3$, which shows considerable ionic character. However, the salts of aluminium and other metals of the group ionize in water to form the tripositive ions, *e.g.*, $Al^{3+}$.

*i. Oxides.* Boron and aluminium directly combine with oxygen to form the oxides $B_2O_3$ and $Al_2O_3$ respectively.

$$4B + 3O_2 \rightarrow 2B_2O_3$$

$$4Al + 3O_2 \rightarrow 2Al_2O_3$$

Boron oxides, $B_2O_3$, is weakly acidic and dissolves in water forming boric acid, a weak acid, in solution.

$$B_2O_3 + 3H_2O \rightarrow 2H_3BO_3 \text{ (boric acid)}$$

Aluminium hydroxide is amphoteric and therefore will dissolve in acid or base to form $Al^{3+}$ or $AlO_2^-$ respectively.

$$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O \text{ (basic character)}$$

$$Al_2O_3 + 2OH^- \rightarrow 2AlO_2^- + H_2O \text{ (acid character)}$$

*ii. Hydroxide.* The hydroxide of boron is boric acid, $B(OH)_3$ or $H_3BO_3$ Aluminium hydroxide is amphoteric.

*iii. Nitrides.* Both boron and aluminium directly combine with nitrogen to form the nitrides BN and AlN. These nitrides are decomposed by water with evolution of ammonia:-

$$BN + 3H_2O \rightarrow H_3BO_3 + NH_3$$

$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3$$

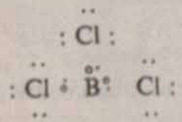
*iv. Halides.* Both boron and aluminium form trihalides of the formula $MX_3$. Except $BI_3$ all the trihalides can be made by heating the elements directly with the halogens.

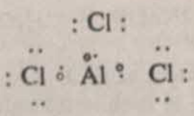
$$2B + 3X_2 \rightarrow 2BX_3;\ X = Cl \text{ or } Br$$

$$2Al + 3X_2 \rightarrow 2AlX_3;\ X = Cl, Br, \text{ or } I$$

Boron trichloride is a fuming liquid, while aluminium chloride is a low melting solid. In aqueous solutions aluminium chloride yields hydrated $Al^{3+}$ ions; boron chloride does not form $B^{3+}$ ions.

In their chlorides, boron and aluminium have only six electrons ($s^2\ p^4$), and are thus two electrons short of the next noble gas configuration ($s^2\ p^6$).





However, up to 500°C or in solutions in inert solvents, aluminium chloride exists in the dimeric form, $Al_2Cl_6$; boron chloride does not dimerize, and exists as $BCl_3$.

## 2. Aluminium in Nature

Aluminium is too active chemically to occur free in nature. In chemical combination, however, it is the most widespread metal in the earth's crust, in which it occurs to the extent of 78 per cent and ranks third among all elements in the order of abundance. It occurs in various minerals as—

(*i*) *oxide* in *corundum* $Al_2O_3$, *bauxite*, $Al_2O_3.2H_2O$, etc.,

(*ii*) *fluoride* in *cryolite*, $Na_3AlF_6$ or $AlF_3.\ 3NaF$.

(*iii*) *basic sulpbate* in *alunite*, $K_2SO_4.Al_2(SO_4)_3.4H_2O$,

(*iv*) *aluminate* in *spinal*, $Mg(AlO_2)_2$ or $MgO.Al_2O_3$, and

(*v*) *silicate* in *kaolin*, *slate*. etc., $Al_2O_3.2SiO_2.2H_2O$.

The principal source of aluminium is bauxite. In India, bauxite is found in Madhya Pradesh, Maharashtra, Tamil Nadu, Bihar, and Kashmir.

## 3. Extraction of Aluminium

Aluminium is extracted from bauxite. This involves three steps :

(1) **Purification of bauxite***. Following processes are in use :

(*a*) *Baeyer's process*. The bauxite is roasted at a low temperature to convert the ferrous oxide into ferric oxide. The roasted bauxite is ground to a fine powder and digested with a hot concentrated solution of sodium hydroxide under pressure. The aluminium oxide of the bauxite passes into solution as sodium aluminate.

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$$

The impurities of ferric oxide, titanium dioxide, and silica remain undissolved and are filtered off.

The filtrate containing dissolved sodium aluminate is diluted and stirred with a little freshly prepared aluminium hydroxide. The impurities of ferric oxide, titanium dioxide, and silica remain undissolved and are filtered off as 'red mud'.

The filtrate containing dissolved sodium aluminate is diluted and stirred with a little freshly prepared aluminium hydroxide ('seeding operation') for several days. This hastens the hydrolysis of sodium aluminate to aluminium hydroxide which is precipitated.

$$NaAlO_2 + 2H_2O \rightarrow Al(OH)_3\downarrow + NaOH$$

The aluminium hydroxide is filtered off and calcined when a high-purity alumina is obtained.

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O\uparrow$$

The filtrate, which is an aqueous solution of sodium hydroxide, is used again for digesting the crude bauxite.

(*b*) *Hall's process*. This process is employed for the purification of low-grade bauxites. Crude bauxite is heated to bright redness with sodium carbonate and limestone. The product, consisting of sodium aluminate, calcium silicate, and unchanged ferric oxide, is treated with water to dissolve out sodium aluminate.

$$Al_2O_3 + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2\uparrow$$
$$SiO_2 + CaCO_3 \rightarrow CaSiO_3 + CO_2\uparrow$$

---

*Serpeck's aluminium nitride process for the purification of bauxite is now obsolete and is nowhere employed.

The water extract is heated to 50—60°C and a stream of carbon dioxide passed through it when aluminium hydroxide is precipitated. This is separated and calcined to obtain alumina.

$$2NaAlO_2 + 3H_2O + CO_2 \rightarrow 2Al(OH)_3 \downarrow + Na_2CO_3$$

The sodium carbonate is recovered and used again.

(2) **Electrolytic reduction of purified alumina dissolved in fused cryolite**. The purified alumina, $Al_2O_3$, is added to molten cryolite contained in a large iron tank lined with gas carbon. Copper plates are moulded into carbon lining to form the electric connection to the cathode. The anodes consists of hard pure carbon blocks which are immersed in molten cryolite (Fig. 10-1). The resistance of the electrolyte to the huge current generates enough heat to keep the substances in molten state at about 1000°C. Aluminium ions are discharged at the cathode and the molten metal, which collects at the base of the cell is drawn off from time to time. When the concentration of alumina falls below a certain level, the resistance of the bath suddenly increases 8-10 times. At this stage, an electric lamp connected across the terminals of the cell begins to glow very brightly. More alumina is now added to the molten electrolyte.

The electrode reactions are :

1. Reduction at cathode : $Al^{3+} + 3e^- \rightarrow Al$
2. Oxidation at anode : $\underset{\text{oxide ion}}{O^{2-}} + C \rightarrow CO + 2e^-$

$$\text{Net reaction} : 2Al^{3+} + 3O^{2-} + 3C \rightarrow 2Al + 2CO$$

The carbon anodes are gradually consumed during the process, and have to be frequently replaced. The crust of the solidified electrolyte and alumina prevents the loss of heat by radiation and the burning of anodes above it. The aluminium obtained is 99·5% pure with traces of iron and silica.

In modern practice, an artificial mixture of the fluorides of aluminium, sodium, and calcium, $2AlF_3.6NaF.3CaF_2$, is used in place of cryolite.

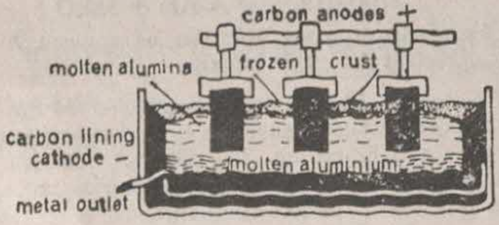


Fig. 10-1. Electrolysis of alumina dissolved in fused cryolite.

(3) **Electrolytic refining of aluminium**. Aluminium of 99·9 per cent purity is obtained by *Hoope's electrolytic* process. It employs a fused bath consisting of three layers in a carbon-lined iron

tank (Fig. 10-2). The densities of these layers are such that their separation is maintained during electrolysis.

(*i*) *The bottom layer* in contact with the carbon lining consists of molten impure aluminium containing copper (to increase its density) and serves as the *anode*.

(*ii*) *The middle layer* consisting of a fused mixture of the fluorides of sodium, aluminium, and barium saturated with aluminium oxide is the *electrolyte*.

(*iii*) *The top layer* is of pure molten aluminium and serves as the *cathode*.

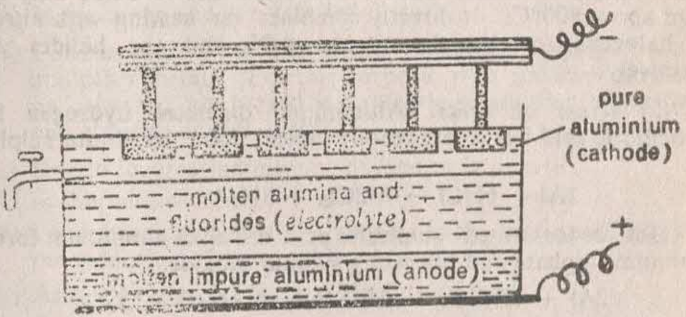

−
pure aluminium (cathode)
molten alumina and fluorides (electrolyte)
+
molten impure aluminium (anode)

Fig. 10-2. Hoope's electrolytic process of refining aluminium.

As electrolysis proceeds. $Al^{3+}$ ions from the middle layer (electrolyte) are discharged into the top layer (cathode) as metallic aluminium. An equivalent amount of aluminium from the bottom layer (anode) passes into the middle layer as $Al^{3+}$, leaving copper, iron, and silicon which are not oxidized under these conditions. Pure aluminium is periodically drawn off from the top layer while molten impure aluminium is added to the bottom layer through a carbon-lined funnel.

## 4. Physical Properties of Aluminium

(1) When freshly cut, aluminium has a silver-white appearance. However, owing to the formation of an oxide film on the surface, it appears dull white in colour. It is capable of taking a high polish.

(2) It is very light (sp. gr. 2.7) and comparatively a soft metal.

(3) It is malleable and ductile and possesses high tensile strength. It is, however, not very tenacious.

(4) It is one of the best conductors of electricity ranking below only silver, copper, and gold in this respect. Weight for weight, it is twice as good a conductor of electricity as copper. That is, an aluminium wire weighs only half as much as a copper wire of equal electrical conductivity.

(5) Aluminium can be welded, cast, or spun. It is, however, not capable of being soldered easily.

(6) It has a fairly high melting point, 657°C, and a very high boiling point, 2056°C.

## 5. Reactions of Aluminium

(1) Although a highly electropositive metal, aluminium is resistant to corrosion. This is due to the thin but tough film of oxide which forms on its surface when it is exposed to moist air, and which protects it from further action. Thus, it is not attacked by air, water, or steam and is converted into its oxide only when heated above 800°C. It directly combines on heating with nitrogen and halogens forming the nitride, $AlN$, and the halides $AlX_3$ respectively.

(2) *Action of acids.* Aluminium displaces hydrogen from hydrochloric acid but is less readily acted upon by dilute sulphuric acid.

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2\uparrow$$

Hot concentrated **sulphuric acid** dissolves aluminium forming aluminium sulphate and liberating sulphur dioxide.

$$2Al + 6H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H_2O + 3SO_2$$

Nitric acid, even when concentrated, not only has no action on aluminium, but even makes it 'passive' so that after treatment with nitric acid it will not dissolve in dilute hydrochloric or sulphuric acid either. This is due to the immediate formation of a highly stable but invisible protective oxide film on the surface.

(3) *Action of alkalis.* Aluminium dissolves in concentrated alkalis forming aluminates and liberating hydrogen.

$$2Al + 2OH^- + 2H_2O \rightarrow 2AlO_2^- + 3H_2{}^*$$

When boiled with a concentrated solution of sodium hydroxide, aluminium gives sodium aluminate and hydrogen.

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2\uparrow$$

(4) *Reducing action.* Aluminium reduces many metallic oxides, *e.g.*,

$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$$

$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$$

(5) *Displacement reactions.* Aluminium displaces less electropositive metals like mercury, silver, gold, etc., from their salts. For example, it displaces mercury from mercuric chloride and dissolves in the displaced mercury forming the amalgam.

$$2Al + 3HgCl_2 \rightarrow 2AlCl_3 + 3Hg$$

---

*The aluminate ion $AlO_2^-$, is hydrated and is probably $[AlO_2(H_2O)_2]^-$ written in the simple form $Al(OH)_4^-$. This equation may, therefore, be written as :

$$2Al + 2OH^- + 6H_2O \rightarrow 2Al(OH)_4^- + 3H_2\uparrow$$

## 6. Uses of Aluminium

(1) Due to its lightness, high tensile strength, resistance to corrosion, and attractive appearance, aluminium is used—

(*i*) For making household utensils.

(*ii*) For the fabrication of industrial plants for food, dairy, and pharmaceutical industries.

(*iii*) In the form of foil for wrapping foodstuff, medicines, etc., and in capping milk bottles.

(*iv*) In the form of powder for making aluminium paints.

(*v*) In buildings and constructional work.

(*vi*) For *calorization*, *i.e.*, for laying aluminium coating on iron and other metals. For this purpose, iron and steel parts to be 'calorized' are heated in a mixture of aluminium powder and alumina at ' 00 –950°C.

(2) Due to its great affinity for oxygen, it is used—

(*i*) In thermite welding.

(*ii*) For preparing corbon-free metals, such as, Cr and Mn by the reduction of their oxides.

(*iii*) As a deoxidizer in the manufacture of steel.

(*iv*) For making certain explosives, *e.g.*, *ammonal* (a mixture of aluminium powder and ammonium nitrate).

(*v*) In flash light bulbs. These contain fine aluminium wire and enough oxygen to burn it completely. The wire burns with an intense white light when ignited by hot filament.

(3) Being good conductor of electrity, it is used for the manufacture of electrical transmission wires.

(4) Being an excellent reflector of light, it is used for making mirrors for reflecting telescopes.

(5) For making alloys, *e.g.*, duralumin, magnalium, alnico, aluminium bronzes, Y-alloy, etc.

### COMPOUNDS OF ALUMINIUM

## 7. Aluminium Oxide, Alumina, $Al_2O_3$

It occurs naturally as bauxite and corundum and also as ruby, emarald, sapphire, etc., which have characteristic colours due to metallic impurities. It can be made by heating the hydroxide strongly :

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O\uparrow$$

It is a white crystalline powder which is extremely hard and infusible, It is an amphoteric oxide. It is used for making refractories and ceramics, and as an abrasive.

## 8. Aluminium Hydroxide, $Al(OH)_3$

It is obtained by adding ammonium hydroxide to a solution of an aluminium salt :

$$3NH_4OH + Al^{3+} \rightarrow Al(OH)_3 \downarrow + 3NH_4^+$$

It is an amphoteric substance due to the following equilibria :

$$Al^{3+} + 3OH^- \rightleftharpoons Al(OH)_3 \rightleftharpoons AlO_2^- + H^+ + H_2O$$

It dissolves in acids forming aluminium salts ($Al^{3+}$) and in alkalis to give aluminates containing the $AlO_2^-$ ion.

$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$$
$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$$

It is used as a mordant for which purpose it is precipitated on the fibres of the cloth which is then dipped into the dyestuff. It is also used for water-proofing cloth.

## 9. Aluminium Chloride, $AlCl_3$ or $Al_2Cl_6$

*Preparation.* When aluminium or its hydroxide is dissolved in hydrochloric acid and the solution is concentrated, colourless crystals of $AlCl_3.6H_2O$ are deposited.

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2 \uparrow$$

When heated, the hydrated aluminium chloride leaves a residue of alumina and does not yield the anhydrous salt.

$$2AlCl_3.6H_2O \rightarrow Al_2O_3 + 9H_2O \uparrow + 6HC \uparrow$$

**Anhydrous aluminium chloride** is made by two methods :

(1) By the action of gaseous or liquid chlorine on aluminium metal.

$$2Al + 3Cl_2 \rightarrow 2AlCl_3$$

The reaction is sufficiently exothermic and the aluminium chloride vaporizes as it is formed.

(2) By strongly heating alumina with carbon and chlorine.

$$Al_2O_3 + 3C + 3Cl_2 \rightarrow 2AlCl_3 + 3CO \uparrow$$

*Properties.* (*i*) Anhydrous aluminium chloride is a white, crystalline, and extremely deliquescent substance. It dissolves freely in organic liquids.

(*ii*) It fumes in moist air owing to the liberation of hydrogen chloride by hydrolysis, and reacts vigorously with water giving an acidic solution for the same reason.

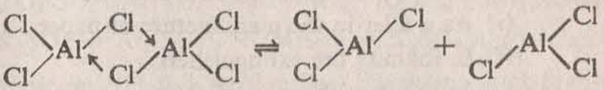
$$AlCl_3 + 3H_2O \leftrightarrows Al(OH)_3 + 3HCl$$

On evaporating the solution, HCl is evolved and aluminium hydroxide is precipitated.

(*iii*) On heating, it sublimes at 183°C. Between 183—400°C its vapour density corresponds to $Al_2Cl_6$ while above 800°C and in solution, its molecular weight corresponds to the formula $AlCl_3$.

(*iv*) It forms addition compounds with substances such as ammonia, phosphine, carbonyl chloride, etc. which can donate a lone pair of electrons. Its addition compound with ammonia corresponds to the formula $AlCl_3.6NH_3$.

*Structure.* Anhydrous aluminium chloride is largely covalent and exists as a *dimer*, $Al_2Cl_6$. In the simple molecule $AlCl_3$, each aluminium atom has six electrons in the outermost shell; these molecules link together in pairs by co-ordinate bonds so that each atom of aluminium may have eight electrons in its outermost shell. The dissociation of the dimeric molecules starts above 400°C and is complete abeve 800°C.



The covalent dimeric structure is retained in non-polar solvents such as, benzene but in aqueous solutions it breaks down into $[Al.6H_2O]^{3+}$ and $3Cl^-$ ions because of the high heat of hydration.

*Uses.* (1) As a catalyst in Friedel-Craft's reaction.

(2) In the cracking of petroleum.

## 10. Aluminium Nitride, AlN

*Preparation.* (*i*) By heating aluminium powder in nitrogen at about 750°C.

$$2Al + N_2 \rightarrow 2AlN$$

(*ii*) By heating alumina with coke and nitrogen.

$$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO\uparrow$$

*Properties.* (*i*) It is a colouless crystalline solid.

(*ii*) It reacts with boiling water or alkalis to yield ammonia.

$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3\uparrow$$

$$AlN + NaOH + H_2O \rightarrow NaAlO_2 + NH_3\uparrow$$

*Use.* Its formation was the basis of the now obsolete Serpeck's process for the fixation of nitrogen of air and for the purification of bauxite.

## 11. Aluminium Sulphate, $Al_2(SO_4)_3$

*Preparation.* By dissolving aluminium or its hydroxide in sulphuric acid. On evaporating the solution, crystals of $Al_2(SO_4)_3.18H_2O$ are obtained.

On a large scale, it is made by the action of hot sulphuric acid on bauxite or China clay.

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O$$

$$\underset{\text{China clay}}{Al_2O_3.2SiO_2.2H_2O} + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 2SiO_2\downarrow + 5H_2O$$

The insoluble substances, *e.g.*, sand, etc. are removed by filtration and the filtrate is evaporated to crystallisation.

*Properties.* Aluminium sulphate is a white crystalline substance which dissolves freely in water. Its aqueous solution is acidic due to hydrolysis. It forms double sulphates, called *alums*, when dissolved in water together with an equivalent amount of an alkali metal sulphate and crystallized.

*Uses.* (*i*) For the purification of water.
(*ii*) As a mordant in dyeing and calico printing*.
(*iii*) In the tanning of leather.
(*iv*) In the water-proofing of cloth**.
(*v*) As a filler in the manufacture of paper.
(*vi*) In foamite fire extinguishers.
(*vii*) In the manufacture of alums.

## 12. Alums

The double sulphates having the general formula

$$M_2SO_4.N_2(SO_4)_3.24H_2O$$

where M is a univalent ion such as $Na^+$, $K^+$, or $NH_4^+$, and N is a trivalent ion such as $Al^{3+}$, $Fe^{3+}$, $Cr^{3+}$ are called alums. For example,

| | |
|---|---|
| $K_2SO_4.Al_2(SO_4)_3.24H_2O$ | *Potash alum* |
| $K_2SO_4.Cr_2(SO_4)_3.24H_2O$ | *Chrome alum* |
| $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$ | *Ammonium alum*, etc. |

These are formed by dissolving equivalent amounts of their component sulphates in hot water and crystallizing. All the alums crystallise in the form of octahedral crystals. Thus all of them are isomorphous. Lithium sulphate is an exception and does not form alums.

**12-1 Potash alum**, $K_2SO_4.Al_2(SO_4)_3.24H_2O$. This is the most common alum and is often called simply alum.

*Preparation.* (1) It may be prepared by crystallization from a saturated solution containing equivalent amounts of potassium sulphate and aluminium sulphate.

(2) By dissolving aluminium foil in the least quantity of caustic potash solution and treating the resulting solution of potassium aluminate with sulphuric acid until it is just acidic. This produces

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*In calico printing, the desired design is printed on the cloth with a solution of the dye containing a mordant and starch or gum. The cloth is then steamed. The metallic hydroxide, *e.g.*, $Al(OH)_3$, adsorbs the dye which will cling permanently to the fabric.

**The cloth is soaked in a saturated solution of alum and then steamed. Aluminium hydroxide resulting from hydrolysis deposits in the capillaries of cotton and makes it waterproof.

$$Al_2(SO_4)_3 + 6HOH \rightarrow 2Al(OH)_3 + 3H_2SO_4$$

equivalent amounts of potassium sulphate and aluminium sulphate in solution which yields common alum upon crystallization.

$$2Al + 2KOH + 2H_2O \rightarrow 2KAlO_2 + 3H_2\uparrow$$

$$2KAlO_2 + 4H_2SO_4 \rightarrow K_2SO_4 + Al_2(SO_4)_3 + 4H_2O$$

(3) It is commercially prepared from the mineral *alunite* or *alumstone*, $K_2SO_4.Al_2(SO_4)_2.4Al(OH)_3$. It is calcined and treated with sulphuric acid when the $Al(OH)_3$ component is also converted into aluminium sulphate. The insoluble impurities are removed by filtration. An additional amount of potassium sulphate is dissolved in the filtrate and the alum allowed to crystallize.

$$K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3 + 6H_2SO_4 \rightarrow K_2SO_4 + 3Al_2(SO_4)_3 + 12H_2O$$

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \rightarrow K_2SO_4.Al_2(SO_4)_3.24H_2O$$

*Properties.* (*i*) It is a colourless crystalline solid, highly soluble in water. The solution contains the ions $K^+$, $Al^{3+}$, and $SO_4^{2-}$ and gives an acidic reaction due to hydrolysis.

$$Al^{3+} + 3HOH \rightleftharpoons Al(OH)_3 + 3H^+$$

(*ii*) On heating, it loses water of crystallization and swells, and finally leaves a residue of *burnt* alum.

$$K_2SO_4.Al_2(SO_4)_3.24H_2O \xrightarrow{\Delta} K_2SO_4 + Al_2(SO_4)_3 + 24H_2O\uparrow$$

*Uses.* Alum is used for the same purposes for which aluminium sulphate is used, *e.g.*, for purification of water, as mordant, for tanning of leather, and as filler in the manufacture of paper. It is also applied externally on cuts to stop bleeding.

## 13. Aluminothermy or Alumino-thermic Process

Aluminium has great affinity for oxygen and combines with it with the libration of much heat.

$$4Al + 3O_2 \rightarrow 2Al_2O_3 + 772{,}000 \text{ cal.}$$

When a mixture of aluminium powder and a metallic oxide (*e.g.*, $Fe_2O_3$) is ignited, a vigorous and highly exothermic reaction occurs and the oxide is reduced to metal.

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe + 199{,}000 \text{ cal.}$$

The large amount of heat set free so suddenly produces a temperature of 3000—3500°C at which the iron and aluminium oxide become liquid. Reactions of this type, called thermite reactions or Goldschmidt reactions after the name of the discover, Hans Goldschmidt, a German chemist, form the basis of the aluminothermic process. This process has two important applications :

(*1*) *For the thermite welding of iron and steel.* A mixture of aluminium powder and ferric oxide, called *thermite*, is placed in a conical converter (Fig. 10-3) lined on the inside with graphite. A small amount of ignition powder consisting of barium peroxide and powdered magnesium is placed in a cavity at the top of the thermite. A fuse of magnesium ribbon is pushed into the ignition powder for starting ignition. The ends of the broken pieces of iron (*e.g.*, of a girder) are placed close together and surrounded by a fireclay mould with a funnel shaped opening at the top.

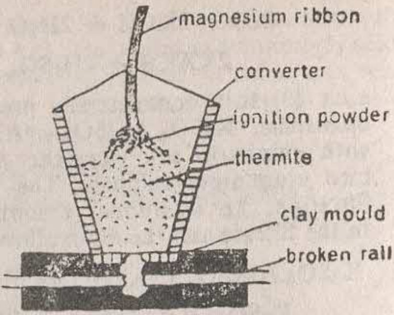


Fig. 10-3. Thermite welding.

When the magnesium ribbon is lighted, the ignition powder catches fire and ignites the thermite. Within a few seconds, the white-hot molten-iron, produced by the reduction of its oxide, flows out from the bottom of the converter welding together the broken ends of the iron object. After solidification, the superfluous iron is trimmed off.

(2) *In the extraction of high melting metals*, such as manganese, chromium, molybdenum etc., from their oxides and in the production of carbon-free metals and alloys.

$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$$

$$3Mn_3O_4 + 8Al \rightarrow 6Mn + 4Al_2O_3$$

## 14. Interconversion of Compounds

Soluble compounds of aluminium can be interconverted into one another through the preparation of aluminium hydroxide by the addition of ammonia solution to a solution of the given aluminium salt. The precipitated aluminium hydroxide is separated by filtration and treated with the appropriate reagent to obtain the desired compound. For example,

$$Al_2(SO_4)_3 \xrightarrow{NH_4OH} Al(OH)_3\downarrow \xrightarrow{HCl} AlCl_3$$

$$AlCl_3 \xrightarrow{NH_4OH} Al(OH)_3\downarrow \xrightarrow{H_2SO_4} Al_2(SO_4)_3$$

### Questions

1. Write the names or formulae of two different types of compounds for aluminium and cerium to justify their position in the periodic table.

2. Discuss the position of aluminium in the periodic table on the basis of its electronic configuration.

3. Aluminium, like boron, is a *p* element. How do you account for the likeness and the difference in their properties on the basis of their electronic configurations.

4. Explain the reason why—

(1) boron is always covalent in its compounds,

(2) $AlF_3$ is ionic while $AlCl_3$ is predominantly covalent in character,

(3) an aqueous solution of aluminium chloride readily attacks a strip of magnesium with the evolution of a gas ?

5. (*a*) Write the name and the formula of the ore from which aluminium is extracted.

(*b*) One of the processes employed for the purification of the ore from which aluminium is extracted is called Baeyer's process. Write the three main operations of this process and give a balanced chemical equation for each operation.

(*c*) Describe how aluminium is produced from the purified ore (technical details are not required).

(*d*) Give *two* properties of aluminium and *two* uses based on the properties you have given.

6. Starting from aluminium chloride how would you obtain the following : (1) aluminium hydroxide, (2) aluminium oxide, and (3) aluminium sulphate. Give equations.

7. What happens when—

*i*. aluminium reacts with sodium hydroxide solution,

*ii*. aluminium is placed in copper sulphate solution,

*iii*. aluminium carbide is treated with water,

*iv*. aluminium nitride is treated with water ?

8. (*a*) Give two methods for the preparations of anhydrous aluminium chloride.

(*b*) Describe the important reactions of aluminium chloride.

(*c*) Discuss the structure of aluminium chloride.

9. (*a*) What are alums ? Give the names and formulae of any three alums.

(*b*) Describe the preparation of potash alum from aluminium metal.

(*c*) How is potash alum manufactured from aluminium minerals ?

(*d*) What happens when potash alum is strongly heated ?

10. Write a short note on the aluminothermic process and its applications.

## Key

3. The electronic configuration of boron is $1s^2$, $2s^2 2p^1$, and of aluminium is $1s^2$, $2s^2 2p^6$, $3s^{21} 3p^1$. The identical number of valency electrons in their atoms explains their likeness, while the difference in the structure of the next to the outermost shells and the size of the atoms, and especially the presence of vacant outermost shells and the size of the atoms, account for the differences in their properties. 3*d* orbitals in aluminium atoms, account for the differences in their properties.

4. (1) Boron has a high ionization energy and its atom is very small.

(2) As compared to the small $F^-$ ion, the much larger $Cl^-$ ion is greatly polarized by the $Al^+$ ion.

(3) An aqueous solution of aluminium chloride contains hydrochloric acid formed by hydrolysis.

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl$$

It therefore reacts with magnesium with the evolution of hydrogen gas.

$$Mg + 2HCl \rightarrow MgCl_2 + H_2 \uparrow$$

5. (*b*) The three operations are :

*i*. The ore is treated with hot concentrated sodium hydroxide solution.

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$$

*ii*. The resulting solution (filtrate) is agitated with water and a small quantity of freshly precipitated aluminium hydroxide (*seeding*).

$$NaAlO_2 + 2H_2O \rightarrow Al(OH)_3 \downarrow + NaOH$$

*iii*. The precipitate of aluminium hydroxide is strongly heated to obtain aluminium oxide.

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O \uparrow$$

(*c*) Purified bauxite is dissolved in fused cryolite, $Na_3AlF_6$, and electrolysed in a large iron tank lined with gas carbon (cathode) using pure carbon bricks as anodes. The $Al_3^{+}$ ions are reduced to aluminium at the cathode.

$$Al^{3+} + 3e^- \rightarrow Al \text{ (at cathode)}$$

$$O^{2-} + C \rightarrow CO + 2e^- \text{ (at carbon anode)}$$

Or, $2Al^{3+} + 3O^{2-} + 3C \rightarrow 2Al + 3CO \uparrow$

# 11

# Elements of Group IVA

## (Silicon and Lead)

In the periodic table, the elements of Groups IA and IIA at the extreme left show strong electropositive, metallic character. while elements of Groups VIA and VIIA at the extreme right show strong electronegative, non-metallic character. As we proceed inward from these extremes to Groups IIIA and VA, the metallic or non-metallic character, respectively, is still present, though far less pronounced. Here, in Group IVA, the metallic or non-metallic character has reached to its minimum. Thus, the elements carbon and silicon of group IVA represent a transition from the metals of group IA, IIA, and IIIA to non-metals of groups VA, VIA, and VIIA in the second and the third period respectively :

| Group ↓ | IA | IIA | IIIA | IVA | VA | VIA | VIIA |
|---|---|---|---|---|---|---|---|
| Period 2 → | Li | Be | B | C | N | O | F |
| Period 3 → | Na | Mg | Al | Si | P | S | Cl |
| | | | | Ge | | | |
| | Electropositive metallic elements | | | Sn | Electronegative non-metallic elements | | |
| | | | | Pb | | | |

As with the Group IIIA elements, this group of elements goes from typical non-metals, C and Si, to typical metals, Sn and Pb, with Ge placed in between as a metalloid—sort of a transition from the non-metals to metals.

## 1. Position of Group IVA Elements in Periodic Table

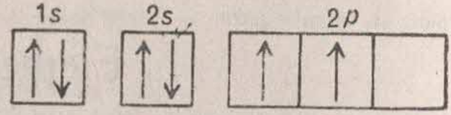
1. **Electronic Configuration.** All of the Group IVA elements are characterised by an outer electron shell containing two *s* and two *p* electrons, *i.e.*, by the $ns^2np^2$ ending, which accounts for the likeness in their chemical behaviour.

**Table 11-1** *Electronic configurations of Group IVA elements*

| Element | Symbol | At. No. | Electronic configuration | | |
|---|---|---|---|---|---|
| Carbon | C | 6 | $1s^2, 2s^2\,2p^2$ | Or, [He] | $2s^2\,2p^2$ |
| Silicon | Si | 14 | $1s^2, 2s^2\,2p^6, 3s^2 3p^2$ | Or, [Ne] | $3s^2\,3p^2$ |
| Germanium | Ge | 32 | $1s^2, 2s^2 2p^6, 3s^2 3p^6 d^{10}, 4s^2\,4p^2$ | Or, [Ar] | $3d^{10}, 4s^2\,4p^2$ |
| Tin | Sn | 50 | | Or, [Kr] | $4d^{10}, 5s^2\,5p^2$ |
| Lead | Pb | 82 | | Or, [Xe] | $4f^{14}, 5d^{10}, 6s^2 6p^2$ |

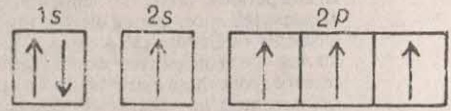
2. **Valency**. The valency commonly shown by the Group IVA elements is +4 for carbon and silicon, and +2 and +4 for Ge, Sn, and Pb. The +4 valency necessitates the unpairing of the *s* electrons of the valence shell and the promotion of one of thsee electrons to the *p* level, thus giving rise to four unpaired electrons.

Electronic structure of carbon atom—ground state



2 unpaired electrons; thus can form two covalent bonds.

Electronic structure of carbon atom—excited state



4 unpaired electrons; thus can form four covalent bonds.

The stability of the +4 valency decreases and that of the +2 valency increases on descending the group. This results from the *s* electrons in the valence shell remaining paired, and not participating in bonding, because the energy to unpair them is too great This phenomenon, called the *inert pair effect*, is quite common particularly among heavy elements in the *p* block.

3. **Type of bonding**. To a large extent, the elements of Group IVA form four-covalent compounds. The divalent compounds of tin and lead are more ionic because the radius of $M^{2+}$ is greater than $M^{4+}$ and according to Fajans rules, the smaller the ion the greater the tendency to covalency. The tetravalent compounds of tin and lead are, therefore, predominantly covalent. The extremely large amount of energy required to form $M^{4+}$ ions suggest that tetravalent ionic compounds will form only with the highly electronegative elements, such as F and O. Thus, the compounds $SnF_4$, $SnO_2$, $PbF_4$, and $PbO_2$ are significantly ionic.

4. **Metallic/nonmetallic character**. The metallic character becomes increasingly more pronounced from carbon to lead. It is reflected in the appearance of the elements, in physical properties such as malleability and electrical conductivity, in the acidic or basic properties of the oxides, and in the increased tendency to form $M^{2+}$ ions.

5. **Chemical reactivity**. The Group IVA elements are relatively inert at room temperature and are not affected by air or water. At high temperatures they take part in many reactions. When heated in air all of them burn to form their oxides. At high temperatures they decompose water in the form of steam, forming their oxides and liberating hydrogen from water. Germanium, tin, and lead displace hydrogen from acids and combine with most nonmetals.

Except carbon, all other elements react with concentrated alkali solutions and liberate hydrogen from them.

$$\underset{\text{}}{Si + 2NaOH + H_2O \rightarrow} \underset{\text{sodium silicate}}{Na_2SiO_3} + 2H_2\uparrow$$

$$Sn + 2NaOH + H_2O \rightarrow \underset{\text{sodium stannate}}{Na_2SnO_2} + 2H_2\uparrow$$

$$Pb + 2NaOH \rightarrow \underset{\text{sodium plumbite}}{Na_2PbO_2} + H_2\uparrow$$

6. **Chemical compounds**. The common compounds of these elements are the oxides, hydrides, and halides.

*i. Oxides.* They all form the monoxide MO, and the dioxides $MO_2$. The common oxides for carbon, silicon, and tin are the dioxides—$CO_2$, $SiO_2$, and $SnO_2$ respectively. However, the stable oxide of lead is the monoxide, PbO. The acidic character of the dioxide decreases as the element increases in atomic number. The oxides and hydroxides of tin and lead are amphoteric. Tin (II) oxide and hydroxide form stannite ion ($SnO_2^{2-}$) upon reaction with a base, and lead (II) oxide and hydroxide form plumbite ion ($PbO_2^{2-}$). The +4 oxides, *i.e.*, $SnO_2$ and $PbO_2$ form stannates ($SnO_3^{2-}$) and plumbates ($PbO_3^{2-}$) respectively upon reaction with bases. The plumbate ion is a powerful oxidizing agent since the +2 valence state is much more stable than the +4 state for lead.

$$Sn(OH)_2 + 2NaOH \rightarrow Na_2SnO_2 + 2H_2O$$
$$Pb(OH)_4 + 2NaOH \rightarrow Na_2PbO_3 + 3H_2O$$

*ii. Hydrides.* All of the Group IVA elements combine with hydrogen to form covalent hydrides of the general formula $MH_4$. This is in marked contrast to the Group IA and IIA elements, which form ionic hydrides.

*iii. Halides.* All of the Group IVA elements form covalent, volatile tetrahalides. These tetrachlorides develop increasing partial ionic character with the rise in the atomic number of the element. Except $CCl_4$, the tetra-halides are readily hydrolysed.

$$SiCl_4 + 3H_2O \rightarrow H_2SiO_3 + 4HCl$$
$$SnCl_4 + 4H_2O \rightarrow Sn(OH)_4 + 4HCl$$
$$PbCl_4 + 2H_2O \rightarrow PbO_2\downarrow + 4HCl$$

Tin and lead also form the dihalides, *e.g*, $SnCl_2$ and $PbCl_2$.

7. **Gradation in properties**. The atomic size, the metallic character, and the chemical reactivity of the elements increases on going down the group, *i.e.*, with the increasing number of the element.

The ease with which the hydrides are formed, and their stability decrease with increasing atomic number. The acidic character of the dioxide and the covalent character of the tetrahalide progressively decreases down the group.

## 2. Position of Silicon in the Periodic Table

Silicon, the second element of group IVA is also the fourth element of the third period of the periodic table. Its neighbours to the left are Na (IA), Mg (IIA), and Al (III) and to the right are P (VA), S (VIA), and Cl (VIIA). Situated in the middle of the electropositive elements on the left and the electronegative elements on the right, silicon displays neither a strong etectropositive character nor a strong electronegative character. The place occupied by silicon in the third period of the periodic table is fully justified on the following considerations :

1. *Valence electrons.* The first element of the third period, sodium, has one valence electron (electronic configuration : 2, 8, 1). The number of valence electrons increases by one in the succeeding elements to become four in silicon, the fourth element, and is seven in chlorine. The maximum valency with respect to hydrogen and oxygen varies in a corresponding manner.

| *Period 3* | Na | Mg | Al | Si | P | S | Cl |
|---|---|---|---|---|---|---|---|
| *Valence electrons* | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| *Maximum valency w.r.t. hydrogen* | 1 | 2 | 3 | 4 | 3 | 2 | 1 |
| *Formula of hydride* | NaH | $MgH_2$ | $AlH_3$ | $SiH_4$ | $PH_3$ | $H_2S$ | HCl |
| *Maximum valency w.r.t. oxygen* | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| *Formula of oxide* | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $Cl_2O_7$ |

2. *Metallic character.* The first three elements of the third period (Na, Mg, and Al) are typical metals. When they are freshly cut, they show the bright lustre of metals. They are good conductors of heat and electricity. The last three elements (P, S, and Cl) are typical non-metals. Silicon, though metallic in appearance, is not a metallic solid. It has the atomic arrangement that occurs in diamond. The silicon crystal is one giant molecule in which each silicon atom is surrounded by, and covalently bonded to, four other silicon atoms. Owing to the absence of mobile electrons, silicon is not a conductor of heat and electricity.

3. *Ionization energy and electronegativity.* The first ionization enery of the third period increases from Na to Cl (with breaks at Al and S); the ionization energy of silicon having intermediate value. The electronegativity regularly increases from Na to Cl; and silicon, situated in the middle, is neither strongly electropositive nor strongly electronegative.

| *Period 3→* | Na | Mg | Al | Si | P | S | Cl |
|---|---|---|---|---|---|---|---|
| *Ionization energy* | 5·1 e.v. | 7·6 e.v. | 6·0 e.v. | 8·9 e.v. | 11·0 e.v. | 10·4 e.v. | 15·7 e.v. |
| *Electronegativity* | strongly electro-positive | electro-positive | less electro-positive | neutral | electro-negative | electro-negative | strongly electro-negative |

4. *Melting point, boiling point, and specific gravity.* The variation in the values of these physical properties fully justifies the position of silicon as the middle element in the third period.

| *Third period→* | Na | Mg | Al | Si | P | S | Cl |
|---|---|---|---|---|---|---|---|
| *M.P.°C* | 98 | 650 | 660 | 1410 | 600 | 119 | —102 |
| *B.P.°C* | 883 | 1100 | 2400 | 2480 | sublimes | 444 | —34 |
| *Sp. gr.* | 0·97 | 1·7 | 2·7 | 2·4 | 2·3 | 2·1 | 1·6 |

5. *Nature of oxide.* Sodium oxide is a strongly basic oxide and combines with water to form the alkali, sodium hydroxide. Magnesium oxides is basic but less strongly so than sodium oxide. Aluminium oxide is amphoteric with the basic character stronger than the acidic character. Silicon dioxide is weakly acidic. The acidic character of the oxides becomes increasingly strong in phosphorus, sulphur, and chlorine.

| *Third period→* | Na | Mg | Al | Si | P | S | Cl |
|---|---|---|---|---|---|---|---|
| *Oxide* | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $Cl_2O_7$ |
| *Nature of oxide* | strongly basic | basic | amphoteric | weakly acidic | acidic | strongly acidic | very strongly acidic |

6. *Oxidizing and reducing strength.* The outstanding chemical character common to metallic sodium, magnesium, and aluminium is the strong reducing power. Silicon cotinues the trend, but is a much weaker reducing agent. Phosphorus shows both reducing and oxidizing properties. Sulphur is essentially an oxidizing agent, and chlorine is a strong oxidizing agent.

7. *Chemical reactivity.* Sodium, the first element of the third period is a highly reactive element and readily forms the monovalent positive ion, $Na^+$. Chlorine represents the other extreme in chemical reactivity, and readily acquires electrons to form monovalent negative ions $Cl^-$. Both of these elements react with water, decomposing it with liberation of hydrogen and oxygen respectively. The chemical reactivity of the sodium type regularly decreases up to silicon while the chemical reactivity of the chlorine type regularly increases from silicon up to chlorine. Silicon is thus a bridge element between the group of the three electropositive elements to the left and the three electronegative elements to the right.

## SILICON, Si

### 3. Silicon in Nature

Silicon does not occur in nature in the free state. In the combined state, principally with oxygen, it is widely distributed in nature, being second only to oxygen in this respect. Silicon comprises nearly one-fourth the mass of the earth's crust and plays as important a part in the mineral kingdom as does carbon in the animal and vegetable kingdoms. Its most common minerals—sand, sandstone, quartz, flint, and rock crystal—consist of silicon dioxide, $SiO_2$; feldspars, mica, clay, asbestos, and many other minerals are silicates. Certain aquatic organisms (*e.g.*, diatoms) have skeletons rich in silica, $SiO_2$, and oat hulls are 40 per cent silica.

## 4. Preparation of Silicon

Silicon forms two allotropic modification—amorphous and crystalline.

**Amorphous silicon** is prepared by the following methods :

(1) By heating silicon in a fireclay crucible with powdered magnesium.

$$SiO_2 + 2Mg \rightarrow Si + 2MgO$$

The product is treated with dilute hydrochloric acid to remove magnesium oxide, unchanged magnesium and magnesium silicide (this is invariably formed in the reduction of silica by magnesium : $SiO_2 + 4Mg \rightarrow Mg_2Si + 2MgO$), and then filtered. Amorphous silicon is left as a dark-brown powder.

(2) By heating silica with crushed coke in an electric furnace (*commercial process).*

$$SiO_2 + 2C \rightarrow Si + 2CO\uparrow$$

Silica must be employed in excess, otherwise the principal product is silicon carbide, SiC ($SiO_2 + 2C \rightarrow SiC + 2CO\uparrow$). The process is operated where hydroelectric power is a available.

**Crystalline silicon** is prepared by the following methods

(1) By reducing silicon tetrachloride with aluminium or zinc at high temperatures; the aluminium chloride or zinc chloride formed volatilizes leaving behind silicon dissolved in the molten metal.

$$3SiCl_4 + 4Al \rightarrow 3Si + 4AlCl_3\uparrow$$

$$SiCl_4 + 2Zn \rightarrow Si + 2ZnCl_2\uparrow$$

(2) By the reduction of silica with aluminium powder by means of the alumino-thermic process.

$$3SiO_2 + 4Al \rightarrow 3Si + 2Al_2O_3$$

In either method, the silicon dissolved in the molten metal is deposited as lustrous, needle-shaped crystals on cooling the melt. The excess metal is removed with dilute hydrochloric acid which leaves the silicon undissolved.

## 5. Physical Properties of Silicon

Although a distinction is often made between the amorphous and crystalline forms of silicon, X-ray analysis shows that the two forms differ only in particle size and purity. It is these two factors which account for their different physical properties and reactivity.

**Amorphous silicon** is a dark brown amorphous powder (sp. gr. about 2·35; m.p. about 1500°C) which does not conduct electricity. It is insoluble in water.

**Crystalline silicon** possesses the diamond structure in which each silicon atom is covalently bonded to four neighbouring silicon atoms at the corners of a regular tetrahedron. Thus a single crystal of silicon is a three-dimensional giant molecule. Crystalline silicon is a dark grey solid with a strong metallic lustre (sp. gravity about 2·5). It is hard enough to scratch glass, but is brittle. It melts at 1420°, and does not dissolve in or react with water.

## 6. Reactions of Silicon

Chemically silicon is rather inert at ordinary temperatures; the crystalline form being still less active. Important reactions of silicon are :

(1) *Burning.* Intense heating causes finely divided silicon to catch fire in air, forming silicon dioxide, $SiO_2$.

$$Si + O_2 \rightarrow SiO_2$$

(2) *Action of acids.* Silicon is very resistant to acids, dissolving only in hydrofluoric acid with the liberation of hydrogen from it. The other product of the reaction, *viz.*, silicon tetrafluoride combines with excess hydrofluoric acid to form hydrofluosilicic acid, $H_2SiF_6$.

$$\begin{array}{l} Si + 4HF \rightarrow SiF_4 + 2H_2 \\ \underline{SiF_4 + 2HF \rightarrow H_2SiF_6 \qquad} \\ Si + 6HF \rightarrow H_2SiF_6 + 2H_2\uparrow \end{array}$$

(3) *Action of alkalis.* Silicon dissolves readily in hot concentrated solutions of alkalis forming silicates in solution and hydrogen.

$$Si + 2NaOH + H_2O \rightarrow \underset{\text{sodium silicate}}{Na_2SiO_3} + 2H_2\uparrow$$

(4) *Combination with halogens.* Silicon combines with fluorine spontaneously and with the other halogens on heating, forming corresponding silicon tetrahalides.

$$Si + 2F_2 \rightarrow SiF_4 \quad \textit{(silicon tetrafluoride)}$$
$$Si + 2Cl_2 \rightarrow SiCl_4 \quad \textit{(silicon tetrachloride)}$$

(5) *Combination with metals and carbon.* Silicon combines with many metals on heating, forming silicides, *e.g.*, magnesium silicide, $Mg_2Si$, and ferrosilicon, FeSi. Heated strongly with carbon, it forms silicon carbide, SiC, also known as *carborundum*.

$$2Mg + Si \rightarrow Mg_2Si$$
$$Si + C \rightarrow SiC$$

## 7. Uses of Silicon

(1) *For making alloys.* Silicon is a constituent of many an important alloys to which it imparts acid resistance and great hardness. The alloy of silicon with iron, called ferrosilicon, is extremely

acid-resistant, and is used for fabricating apparatus for redistilling nitric acid. It is also used as a deoxidizer (*i.e.*, for removing dissolved oxygen) in making castings of steel, copper, and bronze. It is produced by the simultaneous reduction of iron (III) oxide and silica with carbon at about 3000°C in an electric furnace. Another common alloy of silicon, called silicon bronze, is used in the manufacture of telegraph and telephone wires.

(2) *As a semi-conductor.* Very pure silicon is used as a semiconductor in transistors in radio engineering, as well as for solar batteries used in spaceships for transforming solar radiation into electric energy directly.

## 8. Semiconductors

Semiconductors are covalent crystals which at absolute zero would pass no electric current as all the valency electrons would be held by the covalent bonds, but which conduct electricity by the passage of electrons at normal temperatures. At normal temperatures, some of the electrons have sufficient thermal energy to break free from the bonds. These electrons can then migrate, leaving behind a positive charge where a bond is missing. Electrical conduction takes place by the migration of electrons one way, and the migration of 'positive holes' in the other. Germanium and silicon are the most common examples of semiconductors.

The silicon or germanium used as semiconductor must be exceptionally pure (to within 1 part in 1000 million !). This purity is achieved by the technique of *zone refining*. A ring furnace is drawn slowly along a bar of the material, melting a small section as it moves. The impurities in the bar move in front of the melted zone, and are thus pushed to one end of the bar. After purification, carefully controlled amount of some impurity (*e.g.*, arsenic) is added which becomes incorporated in the crystal lattice. This gives a crystal possessing special electrical properties. Silicon treated in this way is used in solar cells to convert sunlight into electrical energy.

## 9. Silicon Dioxide, $SiO_2$

Silicon dioxide, commonly called silica, is the most stable compound of silicon, and is found abundantly distributed in nature both in the crystalline and amorphous varieties. The common crystalline form of silica is *quartz*, a hard, brittle, refractory, colourless solid. *Agate* is a very finely crystalline variety of quartz. Ordinary *sand* consists of tiny grains of quartz, produced in nature by the process of weathering. *Sandstone* consists of sand particles bound together with iron oxide.

Amorphous silica is found in nature as *flint* and *kieselguhr*. Flint consists of amorphous silica associated with quartz. Kieselghur is a mass of hydrated silica formed from skeletons of minute marine organisms called diatoms, and occurs in large deposits in some places.

*Preparation*. Silica can be prepared artificially by the following methods.

(1) By burning silicon in air or still better, in oxygen.

$$Si + O_2 \rightarrow SiO_2$$

(2) By igniting the gelatinous mass of silicic acid produced by decomposing sodium silicate with hydrochloric acid.

$$\underset{\text{sodium silicate}}{Na_2SiO_3} + 2HCl \rightarrow 2NaCl + \underset{\text{silicic acid}}{H_2SiO_3 \downarrow}$$

$$H_2SiO_3 \xrightarrow{\Delta} SiO_2 + H_2O \uparrow$$

*Properties*. (1) Crystalline silica is very hard, insoluble in water. It melts above 1700°C to give a viscous liquid with a random internal structure. On cooling, this liquid undercools and forms a glass, called silica glass. Silica is the only oxide capable of forming an insoluble glass by itself.

(2) *Action of acids*. Silica is attacked only by hydrofluoric acid, yielding silicon tetrafluoride, $SiF_4$.

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

(3) *Action of alkalis*. Silica dissolves in boiling alkali solutions, to form silicates.

$$2NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$$

(4) *As an acidic oxide*. Silica combines with basic oxides at high temperatures forming the salts—silicates. For example,

$$SiO_2 + CaO \rightarrow CaSiO_3 \text{ (calcium silicate)}$$

At high temperatures, silica displaces the more volatile oxides from metallic salts forming corresponding silicates. For example,

$$SiO_2 + Na_2CO_3 \rightarrow Na_2SiO_3 + CO_2 \uparrow$$

$$SiO_2 + Na_2SO_4 \rightarrow Na_2SiO_3 + SO_3 \uparrow$$

$$3SiO_2 + Ca_3(PO_4)_2 \rightarrow 3CaSiO_3 + P_2O_5 \uparrow$$

Of these reactions, the first two are important in glass making and the third in the manufacture of phosphorus.

(6) *With carbon*. When heated with powdered coke in an electric furnace, silica is reduced to silicon if it is in excess or forms silicon carbide if coke is in excess.

$$SiO_2 + 2C \rightarrow Si + 2CO \quad \text{(silica in excess)}$$

$$SiO_2 + 3C \rightarrow SiC + 2CO \quad \text{(coke in excess)}$$

**Uses**. *Sand* is used in great quantities to make mortar and cement, in the manufacture of glass and porcelain, and as an abrasive*.

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*Abrasives are grained or powdered substances of great hardness that are used for rubbing or grinding down surfaces.

*Quartz* is used to make silica glass or quartz glass by melting in an electric furnace, and cooling the melt. Silica glass is highly transparent to both visible and ultraviolet light and so it is used in the manufacture of mercury vapour lamps* and optical instruments used in the ultraviolet region. Powdered quartz is used in the manufacture of silicon carbide (carborundum), silicon tetrafluoride, and sodium silicate, and to make silica bricks used for lining furnaces. Large crystals of quartz are used for lenses of optical instruments (quartz transmits ultraviolet light which is stopped by ordinary glass), and also for controlling the frequency of radio transmitters.

*Sandstone* is used as a building material.

*Kieselguhr*, a very porous and absorbent material, is used for filtering and absorbing various liquids, and in the manufacture of dynamite by absorption of nitroglycerine.

*Agate* is used for knife-edges of laboratory balances, for making mortars for grinding hard materials, and in ornaments.

**Structure**. Silicon dioxide in the form of quartz exists in the form of a giant molecule. Each silicon atom in the giant molecule is in the centre of a tetrahedron with oxygen atoms at its corners, and each oxygen atom linked to two atoms of silicon (Fig. 11-1). Thus, each crystal consists of tetrahedral $SiO_4$ units bonded together covalently by oxygen atoms into a rigid three dimensional, giant silicon-oxygen network. To destroy a quartz crystal a large number of strong bonds between silicon and oxygen atoms must be broken, and this accounts for great hardness high melting point, and chemical inertness of quartz crystal. The overall ratio of silicon to oxygen atoms in the crystal is 1 : 2, but there are no actual molecules of $SiO_2$. The formula $SiO_2$ is merely the simplest formula for the compound; it does not represent a single molecule as does the formula $CO_2$.

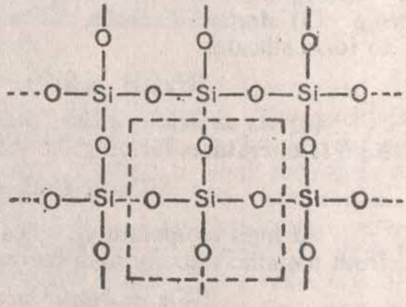

Fig. 11-1. Structure of the silicon dioxide crystal.

In contrast to silica, its carbon analogue, *viz.*, carbon dioxide consists of separate covalent molecules, O=C=O, in which each oxygen atom is attached to the central carbon atom by a double covalent bond. Solid carbon dioxide forms molecular crystals in which independent $CO_2$ molecules occupy the lattice points and are held together by very weak inter-molecular forces. This structure accounts for the softness, low melting point, and volatility of solid carbon dioxide.

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*The radiation from mercury vapour lamps is rich in the ultraviolet region of the spectrum.

## 10. Silicates

Silicon dioxide is an acidic oxide—silicic anhydride, corresponding to *orthosilicic acid*, $H_4SiO_4$ (or, $SiO_2.2H_2O$). The acid cannot be formed by the hydration of silica due to the fact that the latter is very insoluble in water. However, this acid is produced in a colloidal form upon the addition of a strong mineral acid to a solution of an alkali metal silicate or when silicon tetrafluoride, $SiF_4$, is passed into water.

$$3SiF_4 + 4H_2O \rightarrow 2H_2SiF_6 + H_4SiO_4 \uparrow$$

Orthosilicic acid condenses very readily, forming polymeric *metasilicic acid* $(H_2SiO_3)_x$. In simplified form the formula of metasilicic acid is written as $H_2SiO_3$. When silicic acid is formed in any reaction, its composition is usually represented by this formula. The salts of silicic acid are called *silicates*. They can be prepared by fusing silica with metal carbonates or alkalis :

$$SiO_2 + Na_2CO_3 \xrightarrow{\triangle} Na_2SiO_3 + CO_2 \uparrow$$

$$SiO_2 + CaCO_3 \xrightarrow{\triangle} CaSiO_3 + CO_2 \uparrow$$

$$SiO_2 + 2KOH \xrightarrow{\triangle} K_2SiO_3 + H_2O \uparrow, \text{etc.}$$

**10-1. Sodium silicate, $Na_2SiO_3$*.** Commercial sodium silicate is made by fusing silica with sodium hydroxide or sodium carbonate. The glassy product is soluble in water to give a syrupy liquid, called *water glass*. It is used in making soaps and washing formulations to provide an alkaline reaction.

$$SiO_3^- + 2H_2O \rightarrow H_2SiO_3 + 2OH^-$$

It is also used for (*i*) fireproofing and waterproofing fabrics and wooden articles, (*ii*) for the preparation of acidproof cement and concrete, (*iii*) for keroseneproof plasters on concrete, (*iv*) for sizing paper, (*v*) for preserving eggs (it seals their shells with a layer of impervious calcium silicate).

**10-2. Natural silicates.** Silicates are very abundant in nature. They are all very insoluble because of the strength of the Si—O bond, which is only broken by such regents as HF (sodium silicate and potassium silicate, called water glass, are the only soluble silicates). The natural silicates include clays, micas, talc, asbestos, feldspars, and many other minerals.

The natural silicates are all built up of $[SiO_4]^{4-}$ tetrahedra in which four oxygen atoms are arranged tetrahedrally with the silicon

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This formula is a simplification. Actually, sodium silicate has a variable composition, expressed by the generic formula $Na_2O.nSiO_2$.

atom in the middle (Fig. 11-2). The $SiO_4$ tetrahedra link together by sharing the oxygen atoms at the corners between two adjacent tetrahedra in a great variety of structures. The physical properties of natural silicates are largely determined by their crystal structures of which there are three types.

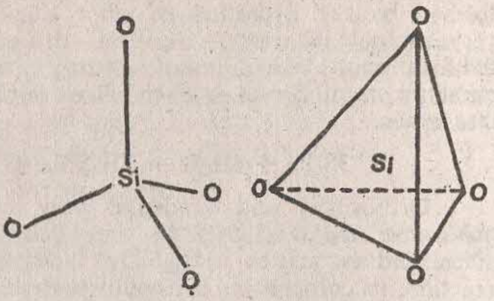


Fig. 11-2. Two representations of the tetrahedral $SiO_4$ group.

(1) When the silicon-oxygen crystal lattice develops in three-dimensional framework the resulting silicate is hard. *Feldspar*, $K(AlSi_3O_8)$ or $K_2O.Al_2O_3, 6SiO_2$, is such a silicate.

(2) When the $SiO_4$ tetrahedra are linked to form sheets, the sheets can be separated with little force. An example of sheet type silicate structure is *mica*, $H_2K(Al_3Si_3O_{12})$ or $K_2O.3Al_2O_3.6SiO_2.2H_2O$, which is split easily into thin sheets (Fig. 11-3).

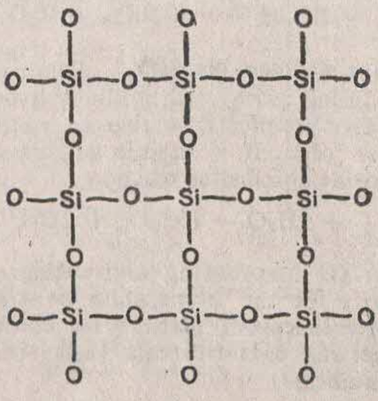


Fig. 11-3. Silicate sheet (example, mica)

(3) In the third type of structure, called the chain structure, the tetrahedra are joined in chains that can be easily separated from one another (Fig. 11-4). The best known example of this type of silicate

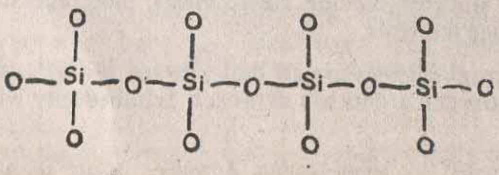


Fig. 11-4. Silicate chain (example, asbestos).

structure is the mineral *asbestos*, $CaMg_3Si_4O_{12}$ or $CaO.3MgO.4SiO_2$, which can be shredded into fibres with remarkable ease.

In *aluminosilicates, e.g.*, feldspar, zeolites, etc., a portion of the tetravalent silicon, $Si^{4+}$, is replaced by the trivalent aluminium, $Al^{3+}$. The negative charge which results is neutralized by a distribution of positive ions such as $Na^+$, $K^+$, or $Ca^{2+}$ throughout the network.

**10-3. Zeolites.** Zeolites, such as $Ca(Al_2Si_7O_{18}).6H_2O$ or $CaO.Al_2O_3.7SiO_2.6H_2O$, are the most important of the three-dimensional silicates. They have honeycomb—like structures which permits them to take up or lose water quite readily from the channels. Other molecules of appropriate size such as $NH_3$, $CO_2$, etc. may also be absorbed instead of water. Thus, zeolites act as *molecular sieves* by absorbing molecules which can enter the channels, but not those which are too big to enter. Zeolites also act as natural cation exchangers. Thus, the calcium and magnesium in the water replace sodium in the zeolites; the process may be reversed and the zeolite restored by washing it with the solution of common salt. The term zeolite is now applied to artificial substances, such as the permutits, used in softening hard water by the 'base-exchange' method.

**10-4. Permutit.** The artificially made sodium aluminosilicates containing varying proportions of soda, alumina, and silica are called *permutits*. These are made by fusing together sodium carbonate, sand, charcoal, and china clay ($Al_2O_3.2SiO_2.2H_2O$) in suitable proportions. The composition of sodium permutit may be represented by the formula $Na_2O.Al_2O_3.4SiO_2\ 2H_2O$.

Permutits possess the property of 'base exchange', *i.e.*, of replacing the sodium ions by other cations, *e.g.*, $Ca^{2+}$, $Mg^{2+}$, etc. Hence, these are used for softening hard water. The base exchange reactions are reversible and attain a state of equilibrium. The base exchange reaction of sodium permutit (formulated as NaP) with $Ca^+$ ions present in hard water may be represented as—

$$Ca^{2+} + 2Na^+P^- \rightarrow Ca^{2+}P_2^{2-} + 2Na^+$$

As the concentration of $Ca^{2+}$ ions increases in the permutit, its activity gradually falls and finally comes to an end when the permutit is said to be exhausted. It is reactivated by treatment with sodium chloride solution when the reverse reaction occurs, regenerating sodium permutit.

$$Ca^{2+}P_2^{2-} + 2Na^+ \rightarrow 2Na^+P^- + Ca^{2+}$$

## 11. Silica Gel

When a solution of a silicate is acidified, a white gelatinous precipitate of silicic acid is slowly formed.

$$Na_2SiO_3 + 2HCl \rightarrow 2NaCl + H_2SiO_3 \downarrow$$

If most of the water is carefully removed (by prolonged drying) from the jelly-like precipitate of silicic acid, a solid product results called *silica gel*.

Silica gel is a white, slightly transluscent solid mass having numerous pores. It posseses excellent adsorption properties, presumably because of its open, porous structure and large surface area per unit of mass. Heat drives off the adsorbed vapour and reactivates hte gel so that it can be used again.

**Uses.** On account of its immense adsorptive capacity, silica gel is used for the following purposes :

(*i*) For adsorbing various gases and vapours, and for recovering valuable vapours from industrial effluents

(*ii*) For removing sulphur compounds, colouring matter, moisture, etc., from petroleum.

(*iii*) For drying the air blast employed in the metallurgy of iron.

(*iv*) As a catalyst in many reactions involving gaseous substances.

(*v*) As a base for finely divided platinum catalyst employed in the contact process for the manufacture of sulphuric acid.

## 12. Silicon Hydrides

**Preparation.** When magnesium silicide, $Mg_2Si$, is treated with dilute hydrochloric acid in the absence of air, monosilane ($SiH_4$) mixed with disilane ($Si_2H_6$), trisilane ($Si_3H_8$), and hydrogen is evolved.

$$Mg_2Si + 4HCl \rightarrow SiH_4 \uparrow + 2MgCl_2$$

**Reactions.** (1) Silanes are not stable to heat, particularly those of higher molecular weights.

(2) They inflame spontaneously in air producing silicon dioxide.

$$SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$$

(3) They explode in contact with oxygen forming silicon tetrahalides, *e.g.*,

$$SiH_4 + 4Cl_2 \rightarrow SiCl_4 + 4HCl$$

(4) They react with alkalis forming silicates and hydrogen.

$$SiH_4 + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 4H_2$$

(5) They are strong reducing agents, reducing ferric salts to ferrous salts and decolorizing potassium permanganate solution.

$$8FeCl_3 + 2H_2O + SiH_4 \rightarrow 8FeCl_2 + 8HCl + SiO_2$$

## 13. Silicon Tetrafluoride, $SiF_4$

**Preparation.** It is made by heating silica (sand) with hydrofluoric, acid, the latter being usually produced in the reaction mixture using powdered calcium fluoride (fluorspar) and excess of concentrated sulphuric acid.

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$$

$$SiO_2 + 4HF \rightarrow SiF_4 \uparrow + 2H_2O$$

**Properties.** (1) Silicon tetrafluoride is a colourless, pungent gas, b.p. −101°C. It fumes in moist air.

(2) It is hydrolysed readily, even by cold water, giving hydrogen fluoride. This is why it corrodes glass when moist.

$$SiF_4 + 3H_2O \rightarrow H_2SiO_3 \downarrow + 4HF$$

The hydrogen fluoride produced combines with unchanged silicon tetrafluoride to give fluorosilicic acid, $H_2SiF_6$, which remains in solution.

$$SiF_4 + 2HF \rightarrow H_2SiF_6$$

**Uses.** Fluorosilicic acid is used for the fluoridation of drinking water. Water containing a few parts of fluorides per million reduces dental decay. It is also used for making fluosilicates for use as insecticides, and as hardening agents in concrete, ceramics, and vitreous enamels.

## 14. Silicon Tetrachloride, $SiCl_4$

Silicon tetrachloride is made by strongly heating a mixture of silica and carbon in a current of dry chlorine.

$$SiO_2 + 2C + 2Cl_2 \rightarrow SiCl_4 + 2CO$$

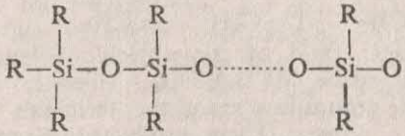
It is a colourless liquid, b.p. 59°C, which fumes in moist air owing to hydrolysis.

$$SiCl_4 + 3H_2O \rightarrow H_2SiO_3\downarrow + 4HCl$$

It is used in the manufacture of silicones.

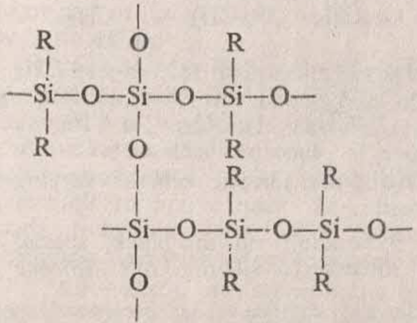
## 15. Silicones

*Silicones are organic silicon polymers composed of chains of alternating silicon and oxygen atoms with alkyl groups attached to the silicon atoms.* The structure may be linear, cross linked, or cyclic :

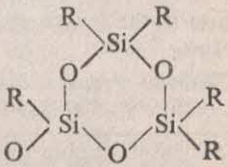


$$R-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O\cdots\cdots O-\underset{R}{\overset{R}{Si}}-O$$

I. Linear type silicone



II. Cross linked type silicone

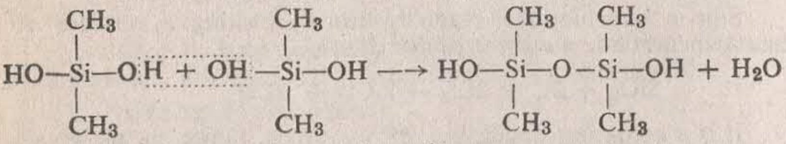


III. Cyclic type silicone

where R stands for a methyl ($CH_3$), ethyl ($C_2H_5$), or a phenyl group ($C_6H_5$).

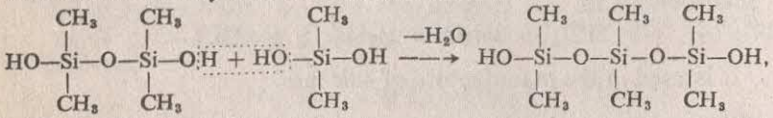
**Preparation.** Silicones are prepared by hydrolyzing alkyl substituted chlorosilanes* followed by progressive condensation of the resulting molecules through the elimination of water molecules. The monochlorosilanes, $R_3SiCl$, give only a dimer; the dichlorosilanes, $R_2SiCl_2$, yield linear and cyclic polymers; while the trichlorosilanes, $RSiCl_3$, with three active groups form cross-linked type (3 dimensional) silicones. For example, the hydrolysis of dimethyldichlorosilane, $(CH_3)_2SiCl_2$, results in the formation of an unstable dihydroxy compound, $(CH_3)_2Si(OH)_2$, which immediately condenses with itself by losing water molecules to finally form a silicone.

$$\underset{\text{dimethyl dichlorosilane}}{(CH_3)_2SiCl_2} + 2H_2O \longrightarrow \underset{\text{unstable silanediol}}{(CH_3)_2Si(OH)_2} + 2HCl$$



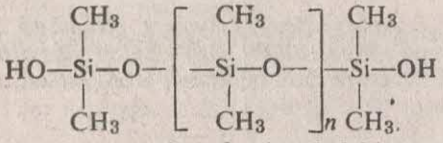
$$HO-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O\,H + OH-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-OH \longrightarrow HO-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-OH + H_2O$$

This is followed by further condensation :



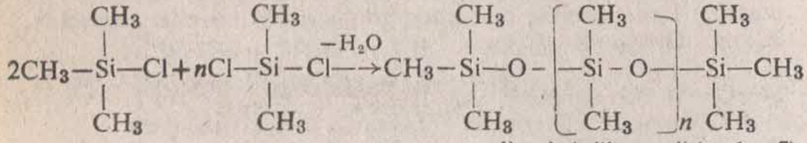
$$HO-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O\,H + HO-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-OH \xrightarrow{-H_2O} HO-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-OH,$$

yielding ultimately the silicone



$$HO-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-\left[-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-\right]_n-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-OH.$$

By using a proper ratio of trimethylchlorosilane. $(CH_3)_3SiCl$, and dimethyldichlorosilane, $(CH_3)_2SiCl_2$, silicones are obtained which contain $-CH_3$ groups in place of the terminal $-OH$ groups in the polymer shown above. These products are called *dimethyl silicone oils*.



$$2CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-Cl + nCl-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-Cl \xrightarrow{-H_2O} CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-\left[-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-\right]_n-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-CH_3$$

dimethyl silicone oil ($n=1$ to 7)

Variation in the length of the chain gives silicone oils of varying viscosities.

*Silicone greases* are made by adding carbon black, special soaps, or finely dispersed silicon dioxide to silicone oils. *Silicone*

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*These are produced by passing the alkyl chloride vapour over powdered silicon containing a little copper as catalyst at 330°C. The resulting mixture consists of monoalkyl trichlorosilane, $RSiCl_3$, dialkyl dichlorosilane, $R_2SiCl_2$, and trialkyltrichlorosilane, $R_3SiCl$, which are separated by fractional distillation.

$$RCl + Si \xrightarrow{Cu,\ \triangle} RSiCl_3 + R_2SiCl_2 + R_3SiCl$$

*resins* are produced by blending silicones with organic resins, such as acrylic esters. *Silicone rubbers* consist of cross-linked type silicones with $SiO_2$ or ZnO as filler and a vulcanizer such as benzoyl peroxide.

**Properties**. The lower silicones are oily liquids, but the higher members, containing long chain or ring structures are waxy and rubbery solids. Silicones are remarkably stable towards heat and chemical reagents, and they are not wetted by water. They are non-toxic and inert chemically. The silicone oils maintain relatively constant viscosity with variations in temperature and, therefore, do not thicken in cold weather.

**Uses**. (1) Silicone oils are used as lubricants, hydraulic fluids, water repellents for textiles and brickwork, and in car, furniture, and floor polishes.

(2) Silicone greases are extremely useful for low temperature lubrication.

(3) Silicone resins are used as electric insulators and for coating metals to prevent atmospheric corrosion and chemical attack.

(4) Silicone rubbers retain their elasticity over a wide range of temperature (from −80°C to 250°C) and have been put to a variety of uses.

(5) A spray coating of a silicone oil on cooking utensils, for example in bakeries, provides a non-stick surface.

## 16. Glass

**16-1. Nature of glass.** Glass is essentially a mixture of silica and various metallic silicates (and sometimes, borosilicates and aluminosilicates, too) which have not crystallized out on cooling from the fused state. Although the silicates of sodium and potassium are solube in water, the glass containing these silicates with other silicates, such as calcium silicate is insoluble in water. Ordinary glass (lime-soda glass) consists of solution of silica in a mixture of sodium and calcium silicates. In other varieties of glasses, potassium may be substituted for sodium, and lead, barium, zinc, and aluminium for all or part of the calcium, while part of the silica may be replaced by boric oxide.

The physical properties of glass are greatly affected by its composition and the proportion of the various constituents. For example, a high proportion of sodium silicate gives a readily fusible glass, whereas the presence of potassium silicate raises the melting point considerably. Glass containing lead silicate has a high density and high refractive index. The presence of about 10 per cent boric oxide produces a glass which is much harder, more resistant to chemicals, and with a very low coefficient of thermal expansion.

All glasses are amorphous, hard, brittle substances, which break with a conchoidal fracture, and are usually transparent. They do not have sharp melting points and begin to soften far below the temperature at which they would flow like a liquid. Molten glass can be blown, moulded, or rolled into sheets. On cooling, gradual hardening occurs, and finally a semi-rigid, brittle solid is formed.

Chemically, glass is rather an inert substance. It is neither affected by water, nor by acids except hydroflouric acid which dissolves it forming flourides and silicon tetrafluoride. Alkalis also attack glass and dissolve its silica forming silicon tetrafluoride.

**16-2. Manufacture of glass.** Glasses are manufactured by fusing the raw materials in regenerative furnaces heated usually by producer gas. The raw materials for making ordinary lime-soda glass are : sodium carbonate or sodium sulphate, limestone or lime, and white sand ($SiO_2$). These are mixed in proper proportion and ground with a certain amount of scrap glass (*cullet*). A charge consisting of this mixture is heated to 1400°C in a large tank lined with fire-brick in a gas fired regenerative furnace. The addition of cullet not merely serves for the utilization of an otherwise waste material, it facilitates the fusion of the charge. During fusion, the following reactions occur :

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2\uparrow$$
$$Na_2SO_4 + SiO_2 \rightarrow Na_2SiO_3 + SO_3\uparrow$$
$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2\uparrow$$

After the evolution of carbon dioxide bubbles ceases, a clear viscous mass results ready for working into finished articles.

**16-3. Coloured glass.** Coloured glass is made by including an appropriate substance in the charge. This additional substance is usually the oxide of some transition metal, *e.g.*, copper, nickel, cobalt, etc., or an elementary substance, *e.g.*, sulphur, gold, copper, etc. In the former case, the colour develops due to the presence of coloured metal ions; in the latter case, due to the formation of colloidal dispersions of the substance added.

**Table 11-2** *Substances used in marking coloured glasses*

| *Substances giving coloured ions* | | *Substances giving colloidal dispersions* | |
|---|---|---|---|
| *Substance* | *Colour* | *Substance* | *Colour* |
| Cupric oxide, cobalt oxide | Blue | Sulphur | Amber |
| Chromic Oxide | Green | Selenium | Ruby red |
| Cuprous Oxide | Red | Silver | Yellow |
| Manganese dioxide | Violet | Calcium fluoride | Milky |

Traces of manganese dioxide are often added during the manufacture of ordinary glass to neutralize the yellow or green colour imparted by the iron oxide impurity in the sand.

**16-4. Varieties of glass.** Some important varicties of glass are :

1. *Soft glass or soda-lime glass.* (Fusion mixture : silica, limestone, and $Na_2CO_3$). It is the ordinary glass and is easily fusible. Of all glasses, it is the least resistant to the solvent action of water. It is used for making window glass, bottles, and cheap glassware.

2. *Hard glass or potash-lime glass.* (Fusion mixture : silica, limestone, and $K_2CO_3$). It is harder, higher melting, and less soluble than soda-lime glass. It is used for making hard glass apparatus capable of withstanding high temperatures.

3. *Optical glass, flint glass, or lead-potassium glass.* (Fusion mixture : silica, red lead, $K_2CO_3$). It is potash-lime glass in which calcium has been replaced by lead. It has a high density and high refractive index, but is less hard. It is used for inexpensive jewellery, 'cut glass' decorative tableware, and optical instruments, such as lenses, prisms, etc.

4. *Pyrex glass.* It is a borosilicate glass contaning up to 12 per cent of boric oxide, with a high silica and low alkai and alumina content. It is more resistant to mechanical shock and temperature change. It is used for making chemical apparatus and high quality tableware.

5. *Jena glass.* It is also a borosilicate glass which differes from pyrex glass in having upto 11 per cent of zinc oxide in place of silica. It is used for making laboratory apparatus.

### LEAD, Pb

## 17. Lead in Nature

Lead is found in nature only in the combined state. Its principal ore is **galena**, PbS, a black, shiny mineral found in many parts of the world. Other minerals of lead are *cerrusite*, $PbCO_3$, and *anglesite*, $PbSO_4$, but these are seldom used in lead metallurgy. The principal lead producing countries are the United States, Spain, and Mexico. In our country, lead-zinc deposites have been located near Udaipur and Jaipur in Rajasthan. These are being exploited by the Metal Corporation of India.

**17-1. Extraction of lead.** Lead is almost exclusively extracted from galena. This mineral invariably contains some silver and zinc as sulphides. The various step in the extraction of lead are :

1. *Concentration of ore.* The ore is crushed, finely ground, and then subjected to mechanical washing to separate gangue (*gravity separation*). Further concentration is achieved by a series of selective floatation processes using different wetting agents.

2. *Roasting.* The concentrated ore is roasted in free supply of air. The sulphide ore provides its own fuel and continues to burn, changing into lead oxide

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2 \uparrow$$

During roasting, the powdered mass sinters into coarse, porous lumps very suitable for charging into the blast furnace for smelting.

3. *Blast furnace smelting*. The roasted sinter is mixed with coke (to serve both as fuel and reducing agent), scrap iron (reducing agent), and limestone (flux) and charged into a blast furnace (Fig. 11-5). A blast of air is sent in through the air blast main for the combustion of coke. The lead oxide is reduced by carbon and carbon monoxide, and the unchanged lead sulphide by the iron, to lead metal.

$$PbO + C \rightarrow Pb + CO\uparrow$$
$$PbO + CO \rightarrow Pb + CO_2\uparrow$$
$$PbS + Fe \rightarrow Pb + FeS$$

Lime, produced from limestone, removes silica as calcium silicate (fusible slag). Also being more basic than lead oxide, it prevents, the formation of lead silicate, $PbSiO_3$.

$$CaO + SiO_2 \rightarrow CaSiO_3 \text{ (slag)}$$

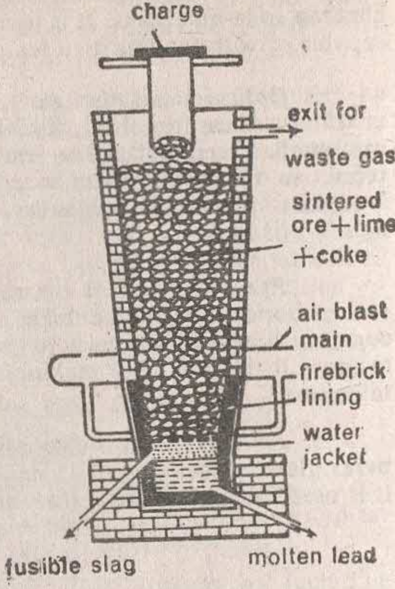

**Fig. 11-5. Blast furnace smelting of lead.**

This process of extraction of lead is known as the *carbon reduction process*. In the older *self reduction process* the lead oxide was reduced to free lead by heating it with more galena.

$$PbS + 2PbO \rightarrow 3Pb + SO_2\uparrow$$

4. *Refining of lead.* The crude lead contains two types of impurities : (*i*) base metals, such as copper, zinc, iron, arsenic, antimony, and bismuth which make it hard and brittle, and (*ii*) silver. These are removed by the following processes :

(*a*) *Fire refining*. The crude molten lead from the blast furnace is transferred to a 'drossing kettle' and agitated by means of compressed air. The metals (except copper) are converted to a scum of oxides on the surface which is skimmed with a perforated disc or spoon. Copper forms a relatively infusible alloy which is separated from the molten lead.

(*b*) *Electrolytic refining* (*Bett's process*). In this process, plates of impure lead are made the anodes and thin sheets of pure lead the cathodes in an electrolytic bath containing lead hexafluosilicate, $PbSiF_6$, and hexafluosilicic acid, $H_2SiF_6$, and gelatin or glue which improves the texture of the lead deposit. On electrolysis, only pure lead is deposited on the cathode; more electropositive impurities remain in solution while less electropositive impurities, such as silver, fall to the bottom of the cell as anode mud.

$$PbSiF_6 \leftrightarrows Pb^{2+} + SiF_6^{2-}$$

## 18. Physical Properties of Lead

(*i*) Lead is a dull grey metal which melts at 327·5°C. When freshly cut it shines with a silvery metallic lustre but rapidly tarnishes in air.

(*ii*) It is soft enough to be easily cut with a knife. It marks paper grey.

(*iii*) It is very malleable and can be rolled into thin sheets and foils It is however, poor in tensile strength and ductility, and cannot be drawn into wire.

(*vi*) It is the heaviest of the common metals except mercury and gold; being 11·4 times as heavy as water.

(*v*) It is a poor conductor of heat and electricty.

## 19. Chemical Properties of Lead

1. *Valency*. Lead exhibits variable valency of +2 and +4. It forms two series of compounds ; the *plumbous* or lead (II) compounds in which the metal is divalent, and the *plumbic* or lead (IV) compounds in which the metal is tetravalent. In case a lead salt is not indicated as lead (II) or lead (IV) salt, it is taken to be a lead (II) or plumbous salt. For example, lead sulphide implies plumbous sulphide, PbS. It also forms negative ions, plumbate ($PbO_3^{2-}$) and plumbite, ($PbO_2^{2-}$).

2. *Action of air*. In the air lead is rapidly tarnished owing to the formation of a superficial white layer of the basic carbonate; this layer is compact and adherent, and protects the metal from further corrosion. On heattng in air, lead combines slowly with oxygen forming lead monoxide, PbO, as a scum. Continued heating in air given red lead, $Pb_3O_4$.

3. *Action of water*. Pure air-free water does not attack lead. Water containing dissolved oxygen, however, dissolves lead very slowly, forming slightly soluble plumbous hydroxide, $Pb(OH)_2$.

$$2Pb + 2H_2O + O_2 \rightarrow 2Pb(OH)_2.$$

Since soluble lead salts are poisonous, the use of lead pipes for conveying water is not safe.

4. *Combination with non-metals*. Lead combines directly with sulphur to form lead sulphide, PbS, and with chlorine to form lead chloride, $PbCl_2$, when heated. It combines directly with carbon and also with nitrogen.

5. *Action of acids*. Lead does not dissolve in dilute hydrochloric acid, nor in dilute sulphuric acid as a coating of the initially formed corresponding insoluble salt (lead chloride and lead sulphate respectively) protects the metal from further action. It dissolves readily in nitric acid, dilute and concentrated, and in acetic acid in the presence of air forming lead nitrate and lead acetate respecti-

vely. Since these salts are soluble, the action of the acid continues and rapid corrosion of lead occurs.

(*i*) $3Pb + 8HNO_3\,(\text{dil.}) \rightarrow 3Pb(NO_3)_2 + 4H_2O + 2NO\uparrow$

(*ii*) $Pb + 4HNO_3\,(\text{conc.}) \rightarrow Pb(NO_3)_2 + 2H_2O + 2NO_2\uparrow$

(*iii*) $2Pb + 4CH_3.COOH + O_2(\text{air}) \rightarrow \underset{\text{lead acetate}}{2Pb(CH_3.COO)_2} + 2H_2O$

With hot concentrated sulphuric acid lead gives sulphur droxide; the reaction continues as lead sulphate is soluble in concentrated sulphuric acid.

$$Pb + 2H_2SO_4\,(\text{hot. conc.}) \rightarrow PbSO_4 + 2H_2O + SO_2\uparrow$$

Lead is attacked slowly by concentrated hydrochloric acid in the cold and rapidly when heated.

$$Pb + 2HCl\,(\text{conc.}) \rightarrow PbCl_2 + H_2\uparrow$$

5. *Action of alkalis.* Lead is not attacked by alkalis.

## 20. Uses of Lead and Its Compounds

The uses of lead depend mainly upon its flexibility, resistance to corrosion, and low melting point. Its chief uses are :

(1) For roofing and plumbing, and for making the sheaths of electric cables in underground wire systems.

(2) For making lead chambers, the housings of towers, the coils of coolers, etc. in sulphuric acid plants and evaporaters in chemical plants.

(3) For the lining of many types of reaction vessels.

(4) For making the negative plates in storage batteries.

(5) In making shots and bullets; for this purpose lead is hardened by alloying with 0·5 per cent arsenic.

(6) As screening agent against radiation, since it is the cheapest among dense metals and a very good absorber of gamma radiations. Lead bricks are used to build screening walls around X-ray generators, small nuclear reactors, etc. Lead containers are used for storing and transporting radioactive isotopes.

(7) For making lead compounds such as litharge and red lead which are used in paints, varnishes, etc., the basic lead carbonate (white lead) which is used as a white pigment, lead tetraethyl which is used in aviation petrol, etc.

(7) As a constituent of several important alloys, *e.g.*, solders, type metal, fuse metals (which melt below 100°C), etc.

**Table 11-3.** *Some important alloys of lead*

| *Name of alloy* | *Composition* | *Main uses* |
|---|---|---|
| 1. Type metal | Pb 82%, Sb 15%, Sn 3% | In making types for printing. |
| 2. Solder | Pb 33%, Sn 67% | In soldering. |
| 3. Fuse metals | | |
| *i.* Rose metal | Bi 50%, Pb 28%, Sn 22% | In making soft solder, safety plugs for boilers and automatic water sprinklers to put out fire, electric fuses, etc. |
| *ii.* Newton metal | Bi 50%, Pb 31%, Sn 19% | |
| *iii.* Wood's metal | Bi 50%, Pb 25%, Sn 12·5%, Cd 12·5%. | |

## 21. Plumbosolvency

Lead does not dissolve in pure air-free water, but it slowly dissolves in water containing dissolved oxygen forming plumbous hydroxide, which is slightly soluble in water.

$$2Pb + 2H_2O + O_2 \rightarrow 2Pb(OH)_2$$

This solvent action of water on lead is called *plumbosolvency.*

As all soluble lead compounds are toxic* the practice of using lead pipes for conveying drinking water is to be avoided. However, the presence of carbonates or sulphates in water prevents the solvent action of water on lead. This is due to the formation of a protective film of the insoluble lead carbonate and lead sulphate on the surface of lead so that the further action of water and the formation of $Pb(OH)_2$ is stopped. Hence, lead pipes may be used for the delivery of hard water (containing $CO_3^{2-}$ and $SO_4^{2-}$) without danger of lead poisoning.

## 22. Oxides of Lead

**22-1. Lead monoxide, PbO.** It is obtained as a yellow powder called *massicot* by gently heating lead in air around 300°C, or by heating the nitrate or carbonate of lead. It is made industrially by blowing air onto the surface of molten lead at 300°C when it is formed as a dense orange mass, called *litharge.*

Lead oxide is insoluble in water but, being an amphoric oxide, dissolves both in acids and alkalis.

$$PbO + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2O$$

$$PbO + 2NaOH \rightarrow \underset{\text{sodium plumbite}}{Na_2PbO_2} + H_2O$$

It is used in making glass, enamels, and lead compounds; in the paint and varnish industry (to catalyse atmospheric oxidation involved in hardening); and in glazing pottery.

**22-2. Red lead, trilead tetraoxide, $Pb_3O_4$.** It is obtained as an orange-red powder by carefully heating lead monoxide in air between 400-500°C. Above this temperature it changes back to lead monoxide.

$$6PbO + O_2 \rightleftharpoons 2Pb_3O_4$$

It is regarded as a mixed oxide, $PbO_2.2PbO$. This is borne out by the fact that when treated with nitric acid, it leaves behind $PbO_2$ as an insoluble residue, while the PbO constituent dissolves to give lead nitrate, $Pb(NO_3)_2$,

$$Pb_3O_4 \text{ (or, } PbO_2.2PbO) + 4HNO_3 \rightarrow PbO_2 + Pb(NO_3)_2 + 2H_2O$$

$$\begin{array}{c}
Pb_3O_4 + 4HCl \rightarrow 2PbCl_2 + PbO_2 + 2H_2O \\
PbO_2 + 4HCl \rightarrow PbCl_2 + 2H_2O + Cl_2 \uparrow \\
\hline
Pb_3O_4 + 8HCl \rightarrow 3PbCl_2 + 4H_2O + Cl_2
\end{array}$$

Similarly, $2Pb_3O_4 + 6H_2SO_4 \rightarrow 6PbSO_4 + 6H_2O + O_2$

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*Lead compounds are eliminated from the body so slowly that small amounts taken internally over long periods ultimately add up to poisonous concentrations. When this stage is reached, the victim suffers from colic fits and paralysis, and may die.

It is used in making protective paint for iron structures (by mixing with linseed oil 1, particularly for objects exposed to the weather such as ships and agricultural machinery, and as an oxidizing agent in the match industry.

**22-3. Lead dioxide $PbO_2$.** It is made from red lead by the action of nitric acid; lead dioxide is left behind as an insoluble chocolate brown powder.

It is a powerful oxidizing agent. It gives up oxygen when heated alone above 300°C, or when heated with concentrated sulphuric acid.

$$2PbO_2 \xrightarrow{300^\circ} 2PbO + O_2\uparrow$$

$$2PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O + O_2\uparrow$$

When it is heated with concentrated hydrochloric acid, the latter is oxidized to chlorine.

$$PbO_2 + 4HCl \rightarrow PbCl_2 + 2H_2O + Cl_2\uparrow$$

It also dissolves in concentrated alkalis forming plumbates. Thus, it is an amphoteric oxide.

$$PbO_2 + 2NaOH \rightarrow \underset{\text{sodium plumbate}}{Na_2PbO_3} + H_2O$$

It is used as a constituent of the anode of the charged lead storage batteries and as an oxidizing agent in match-heads.

## 23. Lead carbonate, $PbCO_3$

The normal lead carbonate, $PbCO_3$, occurs in the mineral *cerrusite*. It may be prepared by the action of sodium hydrogen carbonate on the solution of a lead salt.

$$Pb^{2+} + 2HCO_3^- \rightarrow PbCO_3\downarrow + H_2O + CO_2\uparrow$$

More important commercially is basic lead carbonate, $Pb(OH)_2.2PbCO_3$, known as white lead. It is formed as a white precipitate when sodium carbonate is added to the solution of a lead salt.

$$3Pb^{2+}+3Na_2CO_3+H_2O \rightarrow Pb(OH)_2.2PbCO_3+6Na^++CO_2\uparrow$$

It is made on a large scale by the combined action of oxygen (of air), carbon dioxide, moisture, and acetic acid vapour on metallic lead.

White lead is widely used as a white pigment. Paints made from it are easily applied and possess a high covering power.

## 24. Chlorides of Lead

24-1. *Lead (II) Chloride or plumbous chloride*, $PbCl_2$. This compound is commonly called simply lead chloride. It may be formed by the direct union of elements, or by dissolving lead monoxide in hydrochloric acid, or by mixing solutions containing lead (II) ions, $Pb^{2+}$, and chloride ions, $Cl^-$, when it separates as a white precipitate.

It is very slightly soluble in cold water but dissolves considerably in hot water. It is also soluble in solutions of high chloride concentration forming *tetrachloroplumbate* (II) ions, $PbCl_4^{2-}$.

$$PbCl_2 + 2Cl^- \rightleftharpoons PbCl_4^{2-}$$

24-2. *Plumbic* or *lead* (IV) *chloride*, $PbCl_4$. It may be prepared by passing chlorine through a suspension of $PbCl_2$ in hydrochloric acid.

$$PbCl_2 + Cl_2 \rightarrow PbCl_4$$

It is a dense oily yellow liquid, solidifying at —15°C into a crystalline mass. Water decomposes it completely into lead dioxide and hydrochloric acid : $PbCl_4 + 2H_2O \rightarrow PbO_2 + 4HCl$. It is decomposed on heating into plumbous chloride and chlorine.

$$PbCl_2 \xrightarrow{\Delta} PbCl_2 + Cl_2 \uparrow$$

## 25. Some Other Lead Compounds

25-1. **Lead sulphate or Plumbous Sulphate, $PbSO_4$.** It is formed as a white precipitate when sulphuric acid or soluble sulphate is added to the solution of a lead salt :

$$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4 \downarrow$$

It is almost insoluble in water and in dilute acids, but readily dissolves in concentrated alkali solutions to form plumbites, and in solutions containing an excess of acetate ions forming lead acetate. It also dissolves in concentrated sulphuric acid forming the acid salt $Pb(HSO_4)_2$.

25-2. **Lead nitrate, plumbous nitrate, $Pb(NO_3)_2$.** It may be formed by dissolving lead metal or lead monoxide in nitric acid.

It is a milky-white crystalline compound, readily soluble in water. Unless the aqueous solution contains some nitric acid, hydrolysis occurs and the basic nitrates formed.

$$Pb(NO_3)_2 + H_2O \rightleftharpoons Pb(OH)NO_3 \downarrow + HNO_3$$

It decomposes on heating yielding lead monoxide, nitrogen dioxide, and oxygen :

$$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 \uparrow + O_2 \uparrow$$

25-3. **Lead sulphide, plumbous sulphide, PbS.** It is formed as a black precipitate when hydrogen sulphide is passed through a solution of a lead (II) salt.

$$Pb^{2+} + H_2S \rightarrow PbS \downarrow + 2H^+$$

It occurs in nature in the mineral galena.

25-4. **Lead Chromate, $PbCrO_4$.** It is obtained as a yellow precipitate by mixing solutions containing $Pb^{2+}$ ions and $CrO_4^-$ ions (*e.g.*, lead acetate and potasium chromate solutions).

$$Pb^{2+} + CrO_4^{2-} \rightarrow PbCrO_4 \downarrow$$

It is used as a yellow pigment under the name *chrome yellow* or *lemon chrome*.

When lead chromate is boiled with an alkali solution, it is converted into the basic lead chramate, $PbCrO_4.Pb(OH)_2$, which is used as a red pigment under the name *chrome red*. By mixing the normal lead chromate and the basic lead chromate in varying proportions, pigments of different shades or orange colours are obtained which are used under the name *chrome orange*.

## Questions

1. (*a*) What is the common feature of the electron configuration of the Group IVA elements ?

(*b*) What are the common valencies of the various elements of this group ?

(*c*) Carbon has only two unpaired *p* electrons in its valance shell, yet it is usually tetravalent. How do you account for this ?

(*d*) Carbon and silicon are commonly tetravalent while tin and lead of the same group are usually divalent in their stable compounds. Explain.

(*e*) Of the various oxides of lead—PbO, $Pb_3O_4$, and $PbO_2$, which is the most stable ?

(*f*) Which of the oxides $CO_2$, $SiO_2$, $SnO_2$, and $PbO_2$ is the least acidic ?

2. Justify the position of silicon in the third period on the basis of (1) Its electronic configuration, (2) metallic/non-metallic character, and (3) nature of oxide.

3. (*a*) Give two reactions for the preparation of silicon.

(*b*) How does silicon react with hydrochloric acid and alkalis ?

(*c*) Give two main uses of silicon.

(*d*) How is silicon refined for use as a semiconductor ?

4. (*a*) How would you prepare a simple of silica from sodium silicate ?

(*b*) What happens when silica is heated with a concentrated alkali solution.

(*c*) Give the names and uses of any three forms of natural silica.

5. Solid $CO_2$ is a soft volatile solid, while $SiO_2$ is a very hard solid having a high melling point. Explain why it is so.

6. (*a*) Write equations for the reactions that occur when silica is fused with sodium carbonate and calcium carbonate.

(*b*) What is water glass ? How is it made ? Give its important uses.

(*c*) Draw sketches for the three main types of structures of natural silicates.

(*d*) What are the zeolites ? What are their important characteristics ?

7. Write short explanatory notes on any two of the following.

(1) Silica gel
(2) Silicones
(3) Glass
(4) Semiconductors

8. (*a*) Describe the chemical nature of glass. How do the physical properties of soda-lime glass, potash-lime glass, and glass containing lead silicate differ ?

(*b*) What are the raw materials for the production of soda-lime glass ? How is this material prepared ? Give equations for the main reactions that occur. How can red colour be imparted to the glass ?

9. (*a*) Give the names and formulae of three important minerals of lead. Which of these is commonly used for the extraction of the metal ?

(*b*) How is lead extracted from its sulphide ore ? Give equations.

(*c*) How is lead refined electrolytically ?

(*d*) List six uses of lead (excluding alloys).

10. Explain the reason why—

(*a*) lead slowly dissolves in water containing dissolved oxygen,

(*b*) lead does not dissolve in dilute hydrochloric acid or dilute sulphuric acid, and

(*c*) $Pb_3O_4$ is regarded as a mixed oxide ?

11. (*a*) Describe in brief the methods of preparation, important reactions, and uses of any two of the various oxides of lead.

(*b*) Give the chemical name and formula of white lead.

(*c*) Give the chemical names and formulae of three other lead compounds which are used as pigments in paints.

## Key

1. (*a*) The presence of 2*s* and 2*p* electrons in the valence shell.

(*b*) +4 for C and Si; +2 and +4 for Ge, Sn, and Pb.

(*c*) In the excited state, C has four unpaired electron as the *s* electrons are unpaired and one of them is promoted to the *p* sublevel.

(*d*) In tin and lead the two *s* electrons of the valence shell tend to remain unpaired.

(*e*) PbO.

(*f*) $PbO_2$ .

# 12

# Phosphorus

## (An element of group VA)

Group VA of the periodic table is often referred to as the nitrogen family after its first member. The other elements of the group in the order of increasing atomic number are phosphorus, arsenic, antimony, and bismuth. Each of these elements has five valency electrons—two in the *s* and three in the *p* sublevel. All of the family members show a variety of valencies, the most common being −3, +3, and +5.

| Group VA | |
|---|---|
| Element | At No. |
| Nitrogen, N | 7 |
| Phosphorus, P | 15 |
| Arsenic, As | 33 |
| Antimony, Sb | 51 |
| Bismuth, Bi | 83 |

The elements in Group VA vary form typical non-metallic nitrogen and phosphorus to distinctly metallic bismuth, arsenic and antimony sharing the qualities of both non-metals and metals. The change from nonmetallic to metallic behaviour can be seen in their trioxides : $N_2O_3$ and $P_2O_3$ are strongly acidic, $As_2O_3$ and $Sb_2O_3$ are amphoteric, and $B_2O_3$ is definitely basic. The binary compounds of these elements are, with few exceptions, covalent and becoming more polar going down the group; bismuth compounds show partial ionic character. The position of the Group VA as a whole in the periodic table has been discussed at length in chapter 12 of volume I of this book. Here we shall review only the position of phosphorus in the periodic table.

## 1. Position of Phosphorus in the Periodic Table

Phosphorus is the second element in Group VA, being preceded by nitrogen and followed by arsenic Its horizontal neighbours are silicon to the left and sulphur to the right (Fig. 12-1). This position of phosphorus in the periodic table is fully justified on the following considerations :

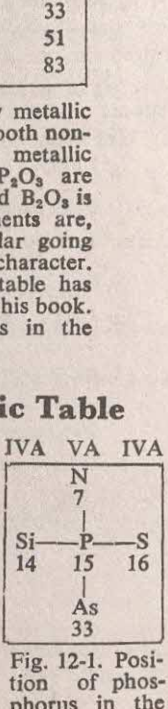


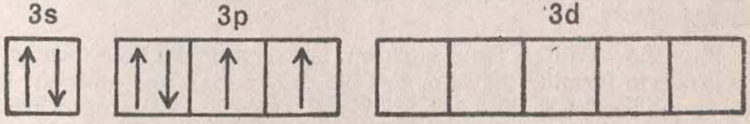
Fig. 12-1. Position of phosphorus in the periodic table.

**1. Electronic configuration.** Phosphorus has five electrons ($3s^2 3p^3$) in its valence shell like all the other elements of Group VA. This is also in agreement with the pattern of the valency electrons regularly increasing across a period; silicon has four valency electrons ($3s^2 3p^2$) and sulphur has six ($3s^2 3p^4$).

**2. Valency.** The principle valencies of phosphorus are +3 and +5 with electronegative elements, *e.g.*, in the oxides, halides, etc., and −3 with hydrogen and strongly electropositive metals, *e.g.*, in phosphine, $PH_3$, and metal phosphides, such as calcium phosphide, $Ca_3P_2$. In the group of elements Si—P—S, the maximum valency varies regularly as +4, +5, and +6 respectively.

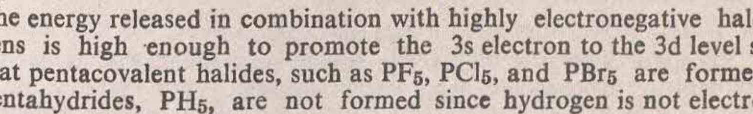
**3. Type of bonding.** Phosphorus, like nitrogen, does not form any positive ion, $P^{3+}$ or $P^{5+}$. However, in combination with strongly electropositive metals, *e.g.*, magnesium and calcium, it forms the negative $P^{3-}$ ion, corresponding to the $N^{3-}$ ion, by gaining three electrons. Like the other elements of Group VA, phosphorus tends to form covalent rather than ionic bonds, and can form both tricovalent compounds and pentacovalent bonds. In the tricovalent compounds the phosphorus atom uses the three unpaired *p* electrons in forming covalent bonds with other atoms; the paired *s* electrons remaining on the phosphorus atom as a lone pair. Pentacovalent compounds are formed when phosphorus atom has five unpaired electrons available for bonding in its excited state as shown below :

Phosphorus atom executed state



3 unpaired electrons;
can form three
covalent bonds.

Phosphorus atom ground slate



five unpaired electrons; can form five covalent bonds

The energy released in combination with highly electronegative halogens is high enough to promote the 3s electron to the 3d level so that pentacovalent halides, such as $PF_5$, $PCl_5$, and $PBr_5$ are formed. Pentahydrides, $PH_5$, are not formed since hydrogen is not electronegative enough to promote the *s* electron.

Nitrogen has no vacant d orbitals in its valence shell (the second shell has only *s* and *p* orbitals); hence, cannot form pentacovalent halides.

**4. Nonmetallic character.** Phosphorus is a typical nonmetal. Justifying its position in the periodic table, it is less nonmetallic and electronegative than nitrogen and sulphur but more so than silicon and arsenic. This is reflected in the acidic character of the oxides of these elements and their oxy-acids.

**5. Compounds**. Phosphorus forms the oxides $P_2O_3$ and $P_2O_5$ which are both acidic and combine with water to give the oxyacids $H_3PO_3$ and $H_3PO_4$ respectively. The acid $H_3PO_4$ is weaker than the corresponding highest oxyacid of nitrogen, *i.e.*, $HNO_3$, but much stronger than that of arsenic $H_3AsO_4$.

Like all other members of the nitrogen family, phosphorus also forms the hydride, $PH_3$, which is a covalent, voltalile substance. The hydride $PH_3$ fits in the general trend of the ease of formation, thermal stability, solubility in water, and the basic character decreasing progressively from $NH_3$ to $BiH_3$. Thus, $PH_3$ is far weaker a base than $NH_3$, and forms phosphonium salts only with strong acids such as HI and HCl under anhydrous conditions ($PH_3 + HI \rightarrow PH_4I$); $SbH_3$, $AsH_3$, and $BiH_3$ are not at all basic.

Phosphorus forms trihalides, $PX_3$, and pentahalides, $PX_5$, both. Phosphorous trihalides are rapidly and completely hydrolysed to give $H_3PO_3$.

$$PX_3 + 3H_2O \rightarrow H_3PO_3 + 3HX$$

Nitrogen is the only element of Group VA which does not form pentahalides owing to the non-availability of vacant *d* orbitals in the valence shell.

Phosphorus differs from nitrogen, but resembles other members of its group in forming the sulphides $P_2S_3$ and $P_2S_5$. The stability of these sulphides $M_2S_3$ and $M_2S_5$ ($M=P$, As, Sb, Bi) progressively increases as we go down the group in conformity with the increasing electropositive character of the element.

## 2. Phosphorus in Nature

Owing to its oxidizing ability, phosphorus does not occur free in nature. It occurs chiefly as calcium phosphate, $Ca_3(PO_4)_2$, in the following minerals :

1. Phosphorite or phosphate rock, $Ca_3(PO_4)_2$.
2. Fluorapatite, $3Ca_3(PO_4)_2.CaF_2$.
3. Chlorapatite, $3Ca_3(PO_4)_2.CaCl_2$.
4. Hydroxyapatite, $3Ca_3(PO_4)_2.Ca(OH)_2$.

Phosphorus plays a vital role in animal and plant life. It is a component of protoplasm, nerve and brain tissue, bone marrow, etc. Hydroxyapatite, $3Ca_3(PO_4)_2.Ca(OH)_2$ is the main mineral constituent of bones and teeth; the skeleton of an average man containing about 2kg of $Ca_3(PO_4)_2$. Phosphorus compounds play an important part in essential energy transformations during photosynthesis and respiration in plants, and in various processes in animal metabolism.

## 3. Preparation of Phosphorus

Phosphorus is prepared by heating well-ground calcium phosphate (phosphate rock), sand, and coke to about 1500°C in a closed electric furnace. To understand the reactions that takes place calcium phosphate may be conceived as a compound of calcium oxide and phosphorus pentoxide ($3CaO.P_2O_5$). The silica displaces the more volatile phosphorus pentoxide, and combining with calcium oxide forms calcium silicate ($CaO.SiO_2$ or $CaSiO_3$); phosphorus pentoxide, is reduced by the carbon to phosphorous.

$$\underset{\substack{\text{calcium phosphate}\\ Ca_3(FO_4)_2}}{2[3CaO.P_2O_5]} + \underset{\text{silica}}{6SiO_2} \rightarrow \underset{\substack{\text{calcium silicated}\\ (CaSiO_3)}}{6(CaO.SiO_2)} + \underset{\substack{\text{phosphorus}\\ \text{pentoxide}}}{P_4O_{10}\uparrow}$$

$$P_4O_{10} + 10C \rightarrow P_4 + 10CO\uparrow$$

Adding up these two equations,

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow P_4{}^* + 6CaSiO_3 + 10CO\uparrow$$

The process is a continuous one. The charge of ground phosphate rock, sand, and coke is continually led into the furnace via the hopper and worm screw feed. The carbon monoxide and the phosphorus, a vapour at the operating temperature, pass through the exit into a condenser. The phosphorus is condensed under water as solid *white phosphorus*. The calcium silicate produced forms a molten slag which is tapped from the furnace (Fig. 12-2).

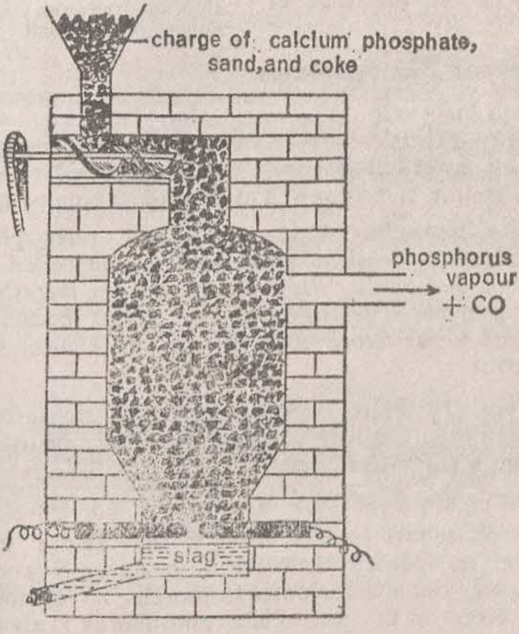


Fig. 12-2. Manufacture of phosphorus from calcium phosphate in an electric furnace.

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*Phosphorus molecules have been shown to be tetra-atomic, both in the vapour form and in the molecular solid form; hence the formula $P_4$.

**3-1. Purification.** The crude phosphorus is purified by melting under a solution of sodium dichromate in sulphuric acid, filtration through canvas, and redistillation in an inert atmosphere. The product is cast in the stick form or block form for packing under water in sealed tins.

## 4. Formula of Phosphorus

Phosphrous molecule consists of four atoms in the vapour form below 700°C*, in the solid state, and in solution in carbon disulphide. The four phosphorus atoms in the molecule are arranged at the corners of a tetrahedron, and linked to each other by single covalent bonds (Fig. 12-3). Hence, phosphorus is represented by the molecular formula $P_4$.

Frequently in equations, however, phosphorus is represented by its symbol P rather than by its molecular formula $P_4$ for the sake of convenience.

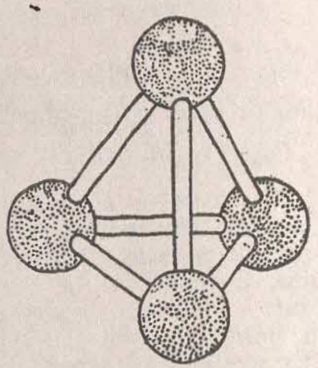

Fig. 12-3. Ball and stick model of $P_4$ molecule ; each ball represents a phosphorus atom ; each stick a single covalent bond.

## 5. Allotropy of Phosphorus

Phosphorus may exist in several allotropic forms which are known according to their colours as white or yellow phosphorus, red phosphorus, and black phosphorus. Of these, however, only the first two forms are the best known, and of practical importance.

**5-1. White phosphorus.** It is produced when phosphorus vapour is condensed or when phosphorus is deposited from its solution in carbon disulphide. White phosphorus is *metastable*, and on long standing acquires a lemon yellow colour because of the partial conversion to the more stable red form. Hence, the name yellow phosphorus.

**Properties.** (1) White phosphorus is a transluscent waxy solid, soft enough to be cut with a knife. However, below 15°C, it is brittle. It has a garlic-like odour.

2. Its specific gravity at 20°C is 1.8.

3. White phosphorus melts at 44°C and begins to boil at 280°C. However, its ignition temperature being only about 35°C, the melting must be done under water to prevent its combustion by contact with oxygen in the air. White phosphorus is always stored under water because of its very low ignition temperature.

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*At higher temperatures, above 700°C. the tetratomic molecules, $P_4$, dissociate into diatomic molecules.

$$P_4 \rightleftharpoons 2P_2$$

4. White phosphorus is insoluble in water, but dissolves readily in carbon disulphide. It is also fairly soluble in chloroform, ether, benzene, and other organic solvents.

5. White phosphorus is very corrosive. It should never be picked up with fingers since it causes very painful burns, slow in healing. It is also very poisonous if taken internally, about 0·1 g being sufficient to cause death. Continued breathing of small amounts of phosphorus vapour causes decay of the bones of the jaw and nose, a condition known as *phossy jaw*.

**5-2. Red Phosphorus**. The change from white to red phosphorus occurs extremely slowly at ordinary temperatures, but rapidly when heated, and is catalysed by the presence of a trace of iodine. Red phosphorus is made industrially by heating white phosphorus with a trace of iodine in the absence of air at about 250°C. The resulting red phosphorus is freed from traces of unchanged white phosphorus and any oxides of phosphorus by boiling it with sodium hydroxide solution.

White phosphorus changes to red form by an exothermic reaction.

$$\textit{White P} \rightarrow \textit{Red P} + \textit{heat}$$

Thus, red phosphorus is at a lower internal energy level than white phosphorus.

Whereas white phosphorus is metastable at all temperatures up to the melting point of red phosphorus, the latter is the stable form. This type of allotropy in which one form is always in the metastable state is called *monotropy* or *monotropic allotropy*. Two chief features of monotropy are :

(*a*) There is no definite transition temperature at which the two solid allotropes are in equilibrium with each other.

(*b*) The direct change from one allotrope to the other can only be made in one direction, from the metastable form to the stable one.

Thus, while the change 'white phosphorus → red phosphorus' occurs spontaneously at all temperatures up to the melting point of red phosphorus, the reverse change, 'red phosphorus → while phosphorus' can be brought about only by converting the red phosphorus into the vapour and then condensing the vapour. The phosphorus vapour, which represents the highest energy state condenses to give white phosphorus, the form having the next highest energy content, and not the red phosphorus which has the lowest energy content.

**Properties.** (1) Red phosphorus is a dark red powder. It has no odour. Its specific gravity is 2·20.

2. When heated in the absence of air, it shows no signs of melting. Rather it sublimes at 400°C and upon cooling turns into

white phosphorus. However, it may be melted under pressure at 592·5°C. Its kindling temperature is 260°C.

3. It is insoluble in water as also in carbon disulphide and all other solvents in which white phosphorus dissolves.

4. It is non-poisonous.

**5-3. Violet phosphorus.** This allotrope of phosphorus is formed by heating a solution of red phosphorus in molten lead to 500°C for some ten hours in the absence of air. The lead is subsequently dissolved away with acids when the violet phosphorus is obtained as violet crystals. This allotrope is also insoluble in carbon disulphide. Its ignition temperature is 260°C.

**5-4. Black phosphorus.** It is formed by heating white phosphorus to 350°C under a pressure of thousands of atmospheres. In appearance it greatly resembles graphite and is greasy to the touch. It is much heavier than the other forms of phosphorus (specific gravity=2·70) and unlike them, conducts electricity well. Its ignition temperature is 490°C.

## 6. Comparison of White and Red Phosphorus

The molecules in white phosphorus consist of units of four atoms linked by single covalent bonds in a tetrahedral arrangement (Fig. 12-4). The molecules in red phosphorus consist of several $P_4$ tetrahedra joined together (Fig. 12-5). On account of such polymerized structure, red phosphorus is much denser that white phosphorus, is insoluble in carbon disulphide in which white phosphorus readily dissolves, and is chemically much less reactive than white phosphorus.

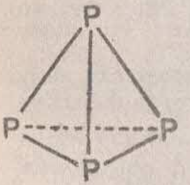

Fig. 12-4. $P_4$ molecule in white phosphorus.

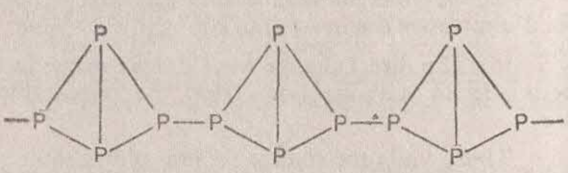

Fig. 12-5. Polymerized structure of red phosphorus consisting of several $P_4$ tetrahedra joined together.

## 7. Reactions of Phosphorus

The two principal forms of phosphorus, *viz.*, white phosphorus and red phosphorus undergo the same chemical reactions on the whole; there is difference only in the rate of reaction. In general, the reactions of red phosphorus are less vigorous.

1. **Phosphorescence.** In the air white phosphorus undergoes slow oxidation below its ignition temperature, emitting a greenish glow which is visible in the dark. This effect, called phosphorescence, is not shown by red phosphorous and can be used to detect the presence of traces of white phosphorus. Phosphorescence is undoub-

tedly some form of oxidation reaction in which phosphorus is converted into one or other of its oxides.

2. **Reaction with oxygen**. Phosphorus burns vigorously in oxygen or air giving off thick, white fumes of phosphorus pentoxide.

$$P_4 + 5O_2 \rightarrow P_4O_{10}^*$$

3. **Combination with active non-metals** (*halogens and sulphur*). While phosphorus ignites spontaneously in chlorine and reacts vigorously with bromine, iodine, and sulphur.

$$P_4 + 6Cl_2 \rightarrow 4PCl_3 \text{ (phosphorus trichloride)}$$

$$P_4 + 10Cl_2 \rightarrow 4PCl_5 \text{ (phosphorus pentachloride)}$$

$$P_4 + 3S \rightarrow P_4S_3 \text{ (phosphorus trisulphide)}$$

All these reactions are exothermic. In the sulphur reaction, various sulphides, *e.g.* $P_4S_3$, $P_4S_{10}$; $P_4S_{14}$, etc. may result, depending on the quantities used.

4. **Combination with active metals**. With the more active metals at higher temperatures, phosphorus directly combines to form phosphides, in which phosphorus displays the −3 valence. Some important metal phosphides are sodium phosphide, $Na_3P$, calcium phosphide, $Ca_3P_2$, and aluminium phosphide, AlP.

$$P_4 + 12Na \rightarrow 4Na_3P$$

$$P_4 + 6Ca \rightarrow 2Ca_3P_2$$

$$P_4 + 4Al \rightarrow 4AlP$$

5. **Reducing reactions**. Phosphorus possesses powerful reducing properties. In its reducing reactions, it is oxidized to phosphoric acid, $H_3PO_4$.

$$P_4 + 16H_2O \rightarrow 4H_3PO_4 + 20H^+ + 20e^-$$

(*a*) It reduce solutions of copper salts to metallic copper ; the liberated copper coats the phosphorus ($Cu^{2+} + 2e^- \rightarrow Cu$).

$$\begin{array}{c} P_4 + 16H_2O \rightarrow 4H_3PO_4 + 20H^+ + 20e^- \\ Cu^{2+} + 2e^- \rightarrow Cu]\times 10 \\ \hline P_4 + 10Cu^{2+} + 16H_2O \rightarrow 4H_3PO_4 + 10Cu\downarrow + 20H^+ \end{array}$$

Or, in the molecular form,

$$P_4 + 10CuSO_4 + 16H_2O \rightarrow 4H_3PO_4 + 10Cu\downarrow + 10H_2SO_4$$

(*b*) It reduces hot nitric acid to nitrogen dioxide.

$$\begin{array}{c} 2HNO_3 + 2H^+ + 2e^- \rightarrow 2H_2O + 2NO_2]\times 10 \\ P_4 + 16H_2O \rightarrow 4H_3PO_4 + 20H^+ + 20e^- \\ \hline P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 4H_2O + 20NO_2\uparrow \end{array}$$

6. **Reaction with alkali solutions**. White phosphorus reacts with hot solutions of caustic alkalis forming phosphine and hypophosphites. For example,

$$P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{sodium hypophosphite}}{3NaH_2PO_2} + \underset{\text{phosphine}}{PH_3\uparrow}$$

Red phosphorus does not react with alkali solutions.

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*This compound is usually named diphosphorus pentoxide or, more simply, phosphrous pentoxide after its simplest ratio, $P_2O_5$. However, the molecules actually have the composition $P_{4-10}$.

## 8. Uses of Phosphorus

(1) *In making phosphorus compounds.* Most phosphorus is used to prepare phosphorus compounds such as phosphoric acid, phosphates, hypophosphites (used in tonic medicines), phosphorus chlorides, metal phosphides (used as rat poison), etc.

(2) *In match industry.* Much phosphorus is consumed by the match industry. The *safety-match* head contains antimony sulphide, oxidizing agents such as potassium chlorate or red lead ($Pb_3O_4$), and sometimes sulphur. The striking surface contains a mixture of red phosphorus and powdered glass (for friction). Friction between this surface and the match head heats the phosphorus, which burns and ignites the match.

(3) *As constituent of phosphor bronze*, an alloy of phosphorus, copper, and tin, so resistant to corrosion that it is used in ships' propellers and fittings.

(4) *In petrol and benzene incendiary bombs* (which cause fire) as an igniting agent, and in smoke bombs, tracer bullets, etc.

(5) *In the laboratory.* Red phosphorus is used in the preparation of hydrobromic and hydriodic acids in the laboratory.

## 9. Phosphine, $PH_3$

**Preparation**. Phosphine is prepared by the following methods :

(1) *By boiling white phosphorus with sodium hydroxide solution* in a flask from which the air has been displaced by coal gas*. A

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*This is necessary in view of the fact that the phosphine produced is impure containing hydrogen and diphosphine, $P_2H_4$, which is spontaneously inflammable in air. The gaseous product may be freed from dipospbine by passing through a U-tube immersed in freezing mixture where diposphine condenses to a liquid, and then collected over water. Unless the diphosphine is removed, the bubbles of the gas burst into flame as they reach the surface of the water in the trough producing rings of white smoke (Fig. 12-6). The smoke consists of phosphoric acid, $H_3PO_4$ ($PH_3 + 2O_2 \rightarrow H_3PO_4$).

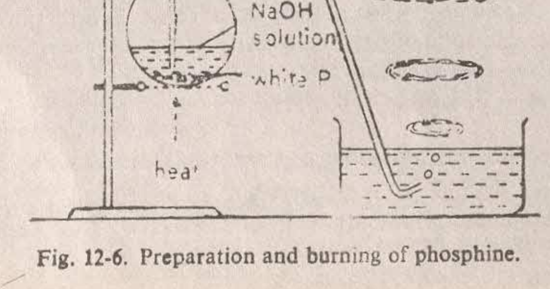

Fig. 12-6. Preparation and burning of phosphine.

solution of sodium hypophosphite is formed and phosphine gas liberated.

$$P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_4 + PH_3\uparrow$$

Pure phosphine may be obtained by using alcoholic caustic potash instead of sodium hydroxide solution.

(2) *By the action of water or dilute acid on calcium phosphide.*

$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3\uparrow$$

The product is usually impure containing hydrogen and diphosphine.

(3) *By the action of caustic soda or caustic potash solution (30 per cent) on phosphonium iodide*, $PH_4I$.

$$PH_4I + NaOH \rightarrow NaI + H_2O + PH_3\uparrow$$

Pure phosphine is formed in this reaction. Phosphonium iodide is made by dissolving phosphorus and iodine in carbon disulphide, evaporating the solution to dryness in a retort from which the air has been displaced by carbon dioxide, and hydrolysing the residue by adding the calculated quantity of water as indicated by the equation—

$$5I + 9P + 16H_2O \rightarrow 5PH_4I + 4H_3PO_4$$

The phosphonium iodide is then separated by sublimation in an atmosphere of carbon dioxide.

(4) *By heating phosphorous acid.* Pure phosphine is obtained in this reaction.

$$\underset{\text{phosphorous acid}}{4H_3PO_3} \xrightarrow{\Delta} \underset{\text{phosphoric acid}}{3H_3PO_4} + \underset{\text{phosphine}}{PH_3\uparrow}$$

**Properties.** Phosphine is a colourless gas which smells like rotting fish. It is highly poisonous. It is twice as heavy as ammonia and only slightly heavier than air (V.D., $PH_3 = 17$, $NH_3 = 8{\cdot}5$, air $= 14{\cdot}4$). It may by liquefied at high pressures and low temperatures to a colourldss liquid, which boils at —87·4°C and freezes at −132°C. Phosphine is only slightly soluble in water (contrast with ammonia which is extremely soluble), and the dissolved phosphine decomposes on standing depositing red phosphorus.

**Reactions.** (1) *Neutral character.* Unlike ammonia, an aqueous solution of phosphine is neutral toward litmus.

2. *Decomposition.* phosphine is decomposed into red phosphorus and hydrogen when heated out of contact with air to 440°C or when electric sparks are passed through it.

$$4PH_3 \rightarrow P_4 + 6H_2$$

3. *Burning.* Phosphine burns vigorously in air to form phosphorus pentoxide, but is not spontaneously inflammable when pure.

$$2PH_3 + 4O_2 \rightarrow P_2O_5 + 3H_2O$$

4. *Reaction with chlorine.* Phosphine ignites spontaneously in chlorine forming phosphorus pentachloride.

$$PH_3 + 4Cl_2 \rightarrow PCl_5 + 3HCl$$

5. *Basic nature.* Though neutral towards litmus, phosphine is feebly basic in nature. Thus, like ammonia, it neutralizes hydrogen halides forming corresponding *phosphonium halides.* For example,

$$PH_3 + HCl \rightarrow PH_4Cl \text{ (phosphonium chloride)}$$
$$PH_3 + HI \rightarrow PH_4I \text{ (phosphonium iodide)}$$

However, phosphine does not combine with water to form phosphonium hydroxide analogous to ammonium hydroxide. Also, the phosphonium halides do not give phosphonium ion, $PH_4^+$, in aqueous solutions corresponding to the ammonium ion, $NH_4^+$, but decompose liberating phosphine.

$$PH_4Cl \rightarrow PH_3\uparrow + HCl \text{ (in aqueous solutions)}$$
$$NH_4Cl \rightarrow NH_4^+ + Cl^- \text{ (in aqueous solutions)}$$

5. *Reducing action.* Phosphine is a powerful reducing agent and will precipitate copper as copper phosphide, and silver and gold as the free metals, when passed through solutions of their salts.

$$3Cu^{2+} + 2PH_3 \rightarrow Cu_3P_2\downarrow + 6H^+$$
$$6Ag^+ + 3H_2O + PH_3 \rightarrow 6Ag\downarrow + 6H^+ + H_3PO_3$$

**Uses.** The spontaneous inflammability of impure phosphine in air is put to the following uses :

(1) *In Holme's signals to the ships.* A mixture of calcium carbide and calcium plosphide is packed in a container and large holes are pierced in it. It is dipped in the sea near a rock. Phosphine liberated by the action of water on calcium phosphide inflammes in air and ignites the acetylene produced by the action of water on the carbide. The light of the burning gases indicates the position of the rock to the approaching ships.

(2) *In making smoke screens in warfare.* Calcium phosphide is made to react with water. The librated phosphine catches fire in air producing heavy smoke.

## 10. Phosphorus Trichloride, $PCl_3$

**Preparation.** Phosphorus trichloride is prepared by passing a current of dry chlorine over white phosphorus, gently warmed to

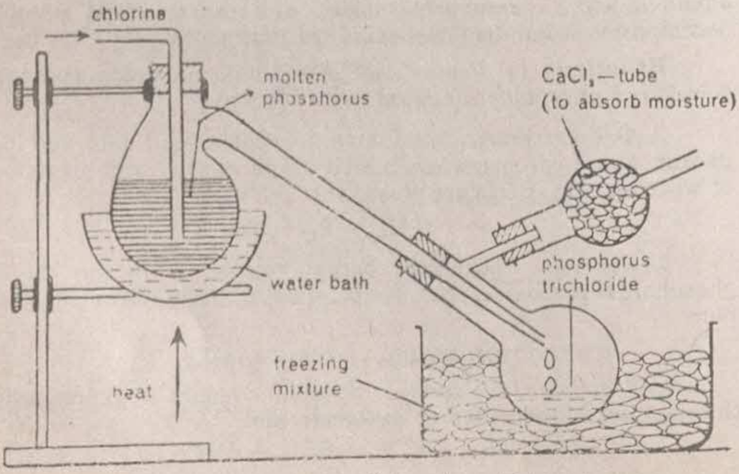

Fig. 12-7. Preparation of phosphorus trichloride.

initiate the reaction, in the complete absence of moisture (Fig. 12-7).

$$2P + 3Cl_2 \rightarrow 2PCl_3$$

The product is purified from any pentachloride formed by distilling it over with white phosphorus.

**Properties.** Phosphorus trichloride is a colourless, pungent smelling liquid, b.p. 76°C, specific gravity 1.6.

**Reactions.** (1) *Hydrolysis.* It is instantly and irreversibly[*] hydrolysed by cold water forming phosphorus acid, $H_3PO_3$.

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

It fumes in moist air due to the formation of hydrogen chloride by hydrolysis.

(2) *Replacement of —OH by —Cl in organic compounds.* It reacts with organic compounds containing hydroxyl group (—OH), *e.g.*, alcohols, carboxylic acids, etc., and replaces the hydroxyl group by a chlorine atom.

$$3[-OH] + PCl_3 \longrightarrow 3[-Cl] + H_3PO_3$$

$$\underset{\text{ethyl alcohol}}{3C_2H_5OH} + PCl_3 \longrightarrow \underset{\text{ethyl chloride}}{3C_2H_5Cl} + \underset{\text{phosphorus acid}}{H_3PO_3}$$

$$\underset{\text{acetic acid}}{3CH_3.COOH} + PCl_3 \longrightarrow \underset{\text{acetyl chloride}}{3CH_3.COCl} + \underset{\text{phosphorus acid}}{H_3PO_3}$$

(3) *Combination with chlorine.* Phosphorus trichloride combines wiih chlorine to form phosphoruss pentachloride.

$$PCl_3 + Cl_2 \rightarrow PCl_5 \text{ (phosphorus pentachloride)}$$

**Uses.** Phosphorus trichloride is used in the preparation of the chloro derivatives of organic hydroxy compounds.

## 11. Phosphorus Pentachloride, $PCl_5$

**Preparation.** Phosphorus pentachloride is formed when phosphorus burns in excess of chlorine ($2P + 5Cl_2 \rightarrow 2PCl_5$). It is conveniently prepared by the action of dry chlorine on phosphorus trichloride.

$$PCl_3 + Cl_2 \rightarrow PCl_5$$

Phosphorus trichloride is admitted dropwise from the funnel into the bottle through which passes a current of dry chlorine. The bottle is kept cool by placing it in freezing mixture (Fig. 12-8). After all the trichloride has been used up, the excess of chlorine is swept out by a current of carbon dioxide, and the bottle corked airtight.

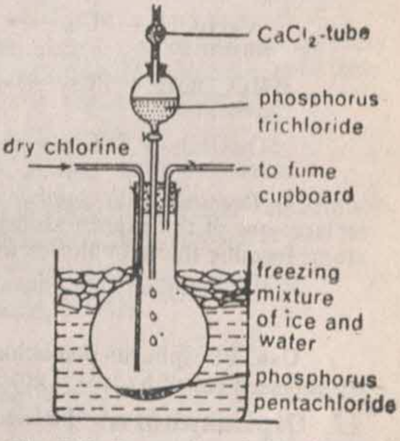

Fig. 12-8. Preparation of phosphorus pentachloride.

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[*] Hydrolysis is usually a reversible process and may be reversed by adding the acid produced in hydrolysis. The hydrolysis of phosphorus trichloride cannot be reversed in this manner.

**Physical properties.** Phosphorus pentachloride is a pale greenish-yellow, hygroscopic solid with a pungent odour. When heated, it sublimes at about 160°C. If heated under pressure, however, it melts at 148°C.

**Reactions.** (1) *Dissociation.* When heated strongly, phosphorus pentachloride dissociates into phosphorus trichloride and chlorine, the percentage dissociation increasing with temperature, and is complete 300°C.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

In accordance with the law of mass action, the dissociation will be suppressed in an atmosphere of chlorine gas.

(2) *Hydrolysis.* Phosphorus pentachloride reacts violently with water. With a *limited amount of cold water*, it is only *partially* hydrolysed yielding phosphorus oxychloride, $POCl_3$, and hydrogen chloride.

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$

With *excess of water*, it is *completely* hydrolysed with the formation of orthophosphoric acid, $H_3PO_4$, and hydrochloric acid.

$$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$$

Phosphorus pentachloride fumes in moist air due to the formation of hydrogen chloride by hydrolysis.

(3) *Replacement of —OH by —Cl in hydroxy compounds.* Phosphorus pentachloride replaces the hydroxyl group by chlorine atom in many organic and inorganic compounds. For example,

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} + PCl_5 \longrightarrow \underset{\text{ethyl chloride}}{C_2H_5Cl} + POCl_3 + HCl$$

$$\underset{\text{acetic acid}}{CH_3.COOH} + PCl_5 \longrightarrow \underset{\text{acetyl chloride}}{CH_3.COCl} + POCl_3 + HCl$$

$$\underset{\text{sulphuric acid}}{SO_2(OH)_2} + 2PCl_5 \longrightarrow \underset{\text{sulphuryl chloride}}{SO_2Cl_2} + 2POCl_3 + 2HCl$$

(4) *Reaction with sulphur dioxide.* Phosphorus pentachloride replaces one of the oxygen atoms in sulphur dioxide by two chlorine atoms forming thionyl chloride and phosphorus oxychloride.

$$SO_2 + PCl_5 \longrightarrow \underset{\text{thionyl chloride}}{SOCl_2} + POCl_3$$

**Use.** Phosphorus pentachloride is used in organic syntheses for the replacement of hydroxyl groups by chlorine atoms.

## 12. Diphosphorus Trioxide, Phosphorus Trioxide, $P_4O_6$

Although the name corresponds to the empirical formula $P_2O_3$, the actual composition of the molecule is $P_4O_6$. It is commonly called phosphorus trioxide and formulated as $P_2O_3$ for convenience.

**Preparation.** It is prepared by burning phosphorus in a limited supply of air.

$$P_4 + 3O_2 \rightarrow P_4O_6$$

The product is freed from phosphorus pentoxide by drawing it through a tube containing a plug of glass wool around which water at 60°C is circulated. Phosphorus pentoxide, solid at 60°C, is held back by the plug of glass wool. The trioxide passes on and is condensed to a white solid in an ice-cooled vessel. (Fig. 12-9).

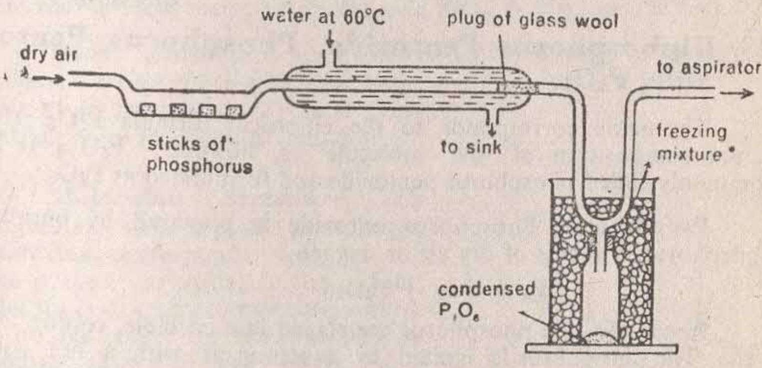


Fig. 12-9. Preparation of phosphorus trioxide.

**Properties.** Phosphorus trioxide is a white crystalline solid, melting at 24°C and boiling at 173°C. It has a garlic-like smell. Its vapour is very poisonous.

**Reactions.** (1) *Oxidation.* On exposure to the air at ordinary temperature, phosphorus trioxide is slowly oxidized to the pentoxide. When heated in air above 60°C, it ignites forming phosphorus pentoxide.

$$P_4O_6 + 2O_2 \rightarrow P_4O_{10}$$

(2) *With chlorine.* It inflames in chlorine at room temperature forming phosphorus oxychloride, $POCl_3$, as the main product.

(3) *As an acid anhydride.* Phosphorus trioxide dissolves slowly in cold water to form phosphorus acid, $H_3PO_3$.

$$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3 \quad (\textit{cold water})$$

With hot water, however, phosphine and phosphoric acid, $H_3PO_4$, are formed due to the decomposition of phosphorus acid.

$$\begin{array}{r} P_4O_6 + 6H_2O \rightarrow 4H_3PO_3 \\ 4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3 \\ \hline P_4O_6 + 6H_2O \rightarrow 3H_3PO_4 + PH_3 \end{array} \quad (\textit{hot water})$$

**Molecular Structure**. The molecular structure of phosphorus trioxide is based on an arrangement of four P atoms at the corners of a tetrahedron (as in the phosphorus molecule). The six oxygen atoms lie along the edges, each in a non-linear P—O—P arrangement curved outward. The structure is shown in Fig. 12-9.

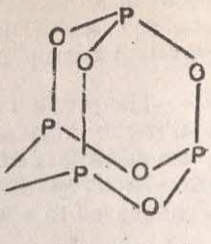


Fig. 12-9. Molecular structure of $P_4O_6$.

## 13. Diphosphorus Pentoxide, Phosphorus Pentoxide, $P_4O_{10}$

The name corresponds to the empirical formula $P_2O_5$. The actual composition of the molecule is, however, $P_4O_{10}$. It is commonly called phosphorus pentoxide and formulated as $P_2O_5$.

**Preparation**. Phosphorus pentoxide is prepared by burning phosphorus in excess of dry air or oxygen.

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

Pieces of white phosphorus are placed in a crucible resting on a tile. The phosphorus is ignited by touching it with a hot wire and immediately covered with a bell jar. The bell jar is slightly lifted from time to time to admit fresh air. White clouds of phosphorus pentoxide are formed which gradually settle down as a snowy white, soft powder.

**Physical properties**. It is a white snow-like solid which is odourless when pure. It sublimes on heating, very slowly at 50°C but more rapidly at high temperatures. It is extremely hygroscopic, and in the air turns rapidly into a sticky mass of metaphosphoric acid.

**Reactions**. (1) *As an acid anhydride*. Phosphorus pentoxide reacts with cold water vigorously, producing a hissing sound and much heat, and forming metaphosphoric acid, $HPO_3$.

$$P_4O_{10} + 2H_2O \rightarrow 4HPO_3$$

With hot water, orthophosphoric acid, $H_3PO_4$, is formed,

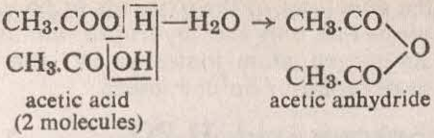
$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

(4) *As a dehydrating agent*. Because of its great affinity for water, phosphorus pentoxide acts as a strong dehydrating agent. It removes the elements of water from a number of inorganic and organic compounds. For example, it dehydrates sulphuric acid into sulphur trioxide (sulphuric anhydride), nitric acid into dinitrogen pentoxide (nitric anhydride), acetic acid into acetic anhydride, and acetamide into methyl cyanide.

$$i.\quad H_2SO_4 - H_2O \rightarrow SO_3$$

ii. $2HNO_3 - H_2O \rightarrow N_2O_5$

iii.



$$\begin{array}{l} CH_3.COO|H \\ CH_3.CO|OH \end{array} - H_2O \rightarrow \begin{array}{l} CH_3.CO \\ CH_3.CO \end{array}\!\!>O$$

acetic acid (2 molecules) — acetic anhydride

iv. $CH_3.CONH_2 - H_2O \rightarrow CH_3.CN$

acetamide — methyl cyanide

(In each case the phosphorus pentoxide combines with the water removed to form metaphosphoric acid $P_2O_5 + H_2O \rightarrow 2HPO_3$).

**Uses.** Phosphorus pentoxide is used (1) as a *drying agent* for all gases, except those which are basic, such as ammonia and (2) as a *dehydrating agent* in chemical reaction.

**Molecular Structure.** The molecular structure of phosphorus pentoxide corresponds to that of phosphorus trioxide, the four additional oxygen atoms being linked by double bonds to the phosphorus atoms as shown in Fig. 12-10. Each phosphorus atom thus shows its higher valency of five.

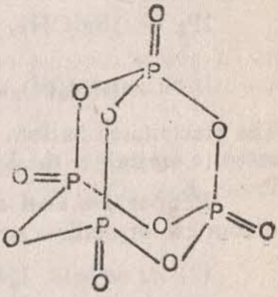


Fig. 12-10. Molecular structure of $P_4O_{10}$.

## 14. Oxy-Acids of Phosphorus

Phosphorus forms two series of oxyacids : **the phosphorous and** the phosphoric series. The important phosphorous **acids** are :

1. Hypophosphorous acid, $H_3PO_2$, and
2. Phosphorous acid, $H_3PO_3(P_4O_6.6H_2O)$.

Phosphorus is in +1 valence state in hypophosphorous acid and in +3 valence state in phosphorous acid. Both of these acids disproportionate, *i.e.*, undergo simultaneous oxidation and reduction, to give phospheric acid ($H_3PO_4$) and phosphine ($PH_3$) respectively upon heating, and are strong reducing agents.

The phosphoric acids are all derived from phosphorus pentoxide, and represent different degrees of hydration depending upon the temperature. The three well-defined phosphoric acids are :

1. Orthophosphoric acid, $H_3PO_4[P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4]$
2. Pyrophosphoric acid, $H_2P_4O_7$ $[P_4O_{10} + 4H_2O \rightarrow 2H_4P_2O_7)$
3. Metaphosphoric acid, $HPO_3$ $[P_4O_{10} + 2H_2O \rightarrow 4HPO_3]$

All of these acids have phosphorus in +5 valence state, the highest for the element. Hence, these acids are not reducing agents.

In considering the structures of the oxyacids of phosphorus, an important point to note is that only the hydrogen atoms linked to phosphorus through an oxygen atom ionise as $H^+$ ions; hydrogen atoms directly liked to phosphorus do not ionize.

## 15. Hypophosphorous Acid, $H_3PO_2$

**Preparation**. Salts of this acid, hypophosphites, are formed in solution when white phosphorus is boiled with alkalis, *e.g.*,

$$P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3\uparrow$$

In the laboratory, hypophosphorus acid is prepared by boiling white phosphorus with barium hydroxide solution and decomosing the resulting barium hypophosphite by adding dilute sulphuric acid.

$$2P_4 + 3Ba(OH)_2 + 6H_2O \longrightarrow \underset{\text{barium hypophosphite}}{3Ba(H_2PO_2)_2} + 2PH_3\uparrow$$

$$Ba(H_2PO_2)_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + 2H_3PO_2$$

The precipitated barium sulphate is filtered off and the filtrate evaporated to crystallize the hypophosphrous acid.

**Properties and reactions**. (1) Hypophosphorous acid is a colourless, crystalline solid, m.p. 26·5°C.

(2) *As an acid*. It is a weak monobasic acid, dissociating as

$$H_3PO_2 \rightleftharpoons H_2PO_2 + H^+.$$

This suggests that of the three hydrogen atom, two are directly linked to the phosphorus atom while one is linked to the phosphorus atom through an oxygen atom.

It forms only one series of salts, the hypophosphites.

(3) *Action of heat*. On heating, the acid decomposes into phosphoric acid and phosphine (disproportionation).

$$2H_3PO_2 \xrightarrow{\Delta} H_3PO_4 + PH_3\uparrow$$

(4) *Reduction*. When treated with zinc and hydrochloric acid (nascent hydrogen), the acid is reduced to phosphine.

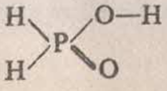
$$H_3PO_2 + 4H \rightarrow 2H_2O + PH_3\uparrow$$

(5) *Reducing action*. Hypophosphorous acid and its salts are powerful reducing agents, and precipitate many metals from the solutions of their salts. For example,

$$H_3PO_2 + 2H_2O + 4Ag^+ \rightarrow H_3PO_4 + 4H^+ + 4Ag\downarrow$$

**Uses**. Salts of hypophosphorus acid, the hypophosphites, are used in tonic medicines.

**Structure**.



## 16. Phosphorous Acid, $H_3PO_3$

**Preparation.** (1) By dissolving phosphorus trioxide in cold water.

$$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$$

(2) By the action of water on phosphorous trichloride.

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

In practice, chlorine is passed into phosphorus melted under water when the phosphorus trichloride formed instantaneously hydrolyses to give phosphorous acid. When all the phosphorus has been used up, the solution is evaporated until the temperature reaches 180°C. On cooling, the acid is obtained as a crystalline solid.

**Properties and reactions.** (1) Phosphorous acid is a white, crystalline, deliquescent solid, m.p. 70·5°C. It has garlic-like odour and is very soluble in water.

(2) *As an acid.* It is a dibasic acid, and forms two series of salts such as sodium *dihydrogen phosphite*, $NaH_2PO_3$ and disodium *hydrogen phosphite*, $Na_2HPO_3$.

$$H_3PO_3 \rightleftharpoons H_2PO_3^- + H^+$$

$$H_2PO_3^- \rightleftharpoons HPO_3^{2-} + H^+$$

The third hydrogen atom is nonionizing. This shows, that of the three hydrogen atoms in its molecule, two are linked to the phosphorus atom through the oxygen atoms and the third one is linked directly to the phosphorus atom.

(3) *Action of heat.* When heated, phosphorous acid undergoes a self oxidation-reduction reaction (disproportionation) to form orthophosphoric acid and phosphine.

$$4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3\uparrow$$

(4) *Reduction.* When treated with zinc and hydrochloric acid (nascent hydrogen), it is reduced to phosphine.

$$H_3PO_3 + 6[H] \rightarrow 3H_2O + PH_3\uparrow$$

(5) *Reducing action.* Phosphorous acid is slowly oxidized in air to phosphoric acid. It is. therefore, a powerful reducing agent ($H_3PO_3 + H_2O \rightarrow H_3PO_4 + 2H^+ + 2e^-$), and precipitates copper, silver, and gold from solutions of their salts, and reduces mercury (II) salts to mercury (I) salts or to mercury.

$$H_3PO_3+H_2O+Cu^{2+} \rightarrow H_3PO_4+2H^++Cu\downarrow$$

$$H_3PO_3+H_2O+2Ag^+ \rightarrow H_3PO_4+2H^++2Ag\downarrow$$

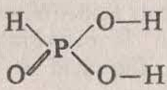
$$H_3PO_3+H_2O+2Hg^{2+} \rightarrow H_3PO_4+2H^++Hg_2{}^{2+}$$

$$[H_3PO_3 + H_2O + \underset{\text{mercuric chloride}}{2HgCl_2} \rightarrow H_3PO_4 + 2HCl + \underset{\text{mercurous chloride}}{Hg_2Cl_2\downarrow}]$$

$$H_3PO_3 + H_2O + \underset{\text{mercurous salt}}{Hg_2{}^{2+}} \rightarrow H_3PO_4 + 2H^+ + \underset{\text{mercury}}{2Hg\downarrow}$$

The phosphites are soluble in water and, like the parent acid, are strong reducing agents.

**Structure**



## 17. Orthophosphoric Acid, $H_3PO_4$

This is the most important of all oxyacids of phosphorus, and it is usually the one meant when phosphoric acid is mentioned.

**Preparation**. (1) By dissolving phosphorus pentoxide in water.

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

(21 By boiling red phosphorus with moderately concentrated nitric acid and a trace of iodine (catalyst).

$$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 4H_2O + 20NO_2\uparrow$$

(3) By the action of dilute sulphuric acid on phosphate rock (calcium phosphate).

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4\downarrow + 2H_3PO_4$$

**Properties and reactions**. (1) Pure orthophosphoric acid is a colourless, crystalline solid, m.p. 42°C. It is extremely deliquescent and absorbs water giving a colourless, syrupy liquid called *syrupy phosphoric acid*, containing 82 per cent $H_3PO_4$. It is in this form that the acid is available commercially.

(2) *As an acid.* It is a weak, tribasic acid which dissociates in solution thus :

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4{}^- \ (\textit{main})$$

$$H_2PO_4{}^- \rightleftharpoons H^+ + HPO_4{}^{2-}$$

$$HPO_4{}^{2-} \rightleftharpoons H^++PO_4{}^{3-}$$

Accordingly, it gives rise to three series of salts : (1) acid salts with two hydrogen atoms in the acid radical, *e.g.*, $NaH_2PO_4$, sodium dihydrogen phosphate, (2) acid salts with one hydrogen atom in the acid radical, *e.g.*, $Na_2HPO_4$, disodium hydrogen phosphate, and (3) normal salts, *e.g.*, $Na_3PO_4$, trisodium or normal sodium phosphate.

(3) *Action of heat.* When heated, orthophosphoric acid progressively loses water to give successively pyrophosphoric acid at 250°C and metaphosphoric acid at 600°C.

$$\underset{\text{orthophosphoric acid}}{2H_3PO_4} \xrightarrow[-H_2O]{250°C} \underset{\text{pyrophosphorie acid}}{H_4P_2O_7} \xrightarrow[-\,H_2O]{600°C} \underset{\text{metaphosphoric acid}}{2HPO_3}$$

These changes are reversible, and the meta- and pyro- acids yield a solution of orthophosphoric acid when boiled with water.

**Uses.** (1) In medicine—as a tonic, as an astringent, and as an antipyretic.

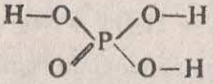
(2) In soft drinks. lemondrops, table jellies, etc. to impart tartness.

(3) In the catalytic conversion of ethyl alcohol to ethylene.

(4) For rust-proofing steel articles before painting.

(5) In the manufacture of phosphates, particularly triple superphosphate and ammonium phosphate, which are used as phosphatic fertilizers (*main use*).

**Structure.** All the three hydrogen atoms in orthophosphoric acid, being ionizable, must be linked to the phosphorus atom through oxygen atoms. Hence, the structure of orthophosphoric acid is



**17-1. Orthophosphates.** The salts of orthophosphoric acid are called orthophosphates, or simply the phosphates. These are termed primary, secondary, or tertiary respectively. according to the number of hydrogen atoms replaced by metal in the acid molecule being 1, 2, or 3. Thus the three sodium salts of orthophosphoric acid are :

(1) Sodium dihydrogen phosphate or primary sodium phosphate, $NaH_2PO_4.H_2O$, Its solution is neutral to methyl orange but acid to phenolphthalein.

(2) Disodium hydrogen phosphate or secondary sodium phosphate. $Na_2HPO_4.12H_2O$. Its solution is neutral to phenolphthalein but alkaline to methyl orange

(3) Trisodium phosphate or normal sodium phosphate, $Na_3PO_4$. Its solution is alkaline to all indicators because of extended hydrolysis.

These salts can be prepared from orthophosphoric acid and sodium hydroxide solution by taking advantage of the fact that methyl orange changes colour at the point when the acid has been completely converted into the primary salt $NaH_2PO_4$, and phenolphthalein changes colour when the conversion into the secondary salt, $Na_2HPO_4$, is complete. No indicator is satisfactory for finding out directly the amount of alkali needed to make the normal salt, $Na_3PO_4$, because its solution is strongly alkaline by hydrolysis. However, the volume of the alkali solution needed to give a solution of the trisodium salt will be thrice as much as that needed to reach the end point with methyl orange, as is clear from the following equations :

$$H_3PO_4 + NaOH\ (x\ ml.) \rightarrow \underset{\text{Methyl orange end point}}{NaH_2PO_4 + H_2O}$$

$$H_3PO_4 + 2NaOH\ (2x\ ml) \rightarrow \underset{\text{Phenolphthalein end point}}{Na_2HPO_4 + 2H_2O}$$

$$H_3PO_4 + 3NaOH\ (3x\ ml) \rightarrow Na_3PO_4 + 3H_2O$$

**Properties.** (1) *Solubility.* All the primary phosphates, *e.g.*, $NaH_2PO_4$, $Ca(H_2PO_4)_2$, etc. are soluble in water, of the secondary and tertiary phosphates only those of sodium, potassium, and ammonium are soluble.

(2) *Action of heat.* When heated the phosphates lose water of crystallization, and swell up. On further heating, primary and secondary phosphates undergo dehydration changing to metaphosphates and pyrophosphates respectively.

$$NaH_2PO_4 \rightarrow H_2O\uparrow + NaPO_3\ \text{(sodium metaphosphate)}$$

$$2Na_2HPO_4 \rightarrow H_2O\uparrow + Na_2P_4O_7\ \text{(sodium pyrophosphate)}$$

Phosphates containing ammonium radical lose both water and ammonia on heating. Thus, sodium ammonium hydrogen phosphate, which occurs in urine and is called microcosmic salt, decomposes to the metaphosphate, ammonia, and water when heated.

$$\underset{\text{microcosmic salt}}{Na(NH_4)HPO_4} \xrightarrow{\Delta} NaPO_3 + NH_3\uparrow + H_2O\uparrow$$

Magnesium ammonium phosphate decomposes thus :

$$\underset{\text{mag. am. phosphate}}{2Mg(NH_4)PO_4} \xrightarrow{\Delta} \underset{\text{mag. pyrophosphate}}{Mg_2P_2O_7} + 2NH_3\uparrow + H_2O$$

**Uses of phosphates.** Phosphates find a wide variety of uses :

(1) *Trisodium phosphate*, $Na_3PO_4$, is used in water softening. Due to its alkalinity in solution and to its emulsifying action, it is used alone, or with soda ash, borax, soap, etc. as a detergent.

(2) *Disodium hydrogen phosphate*, $Na_2HPO_4$, is used as a boiler compound (to prevent scale formation), in weighting silk in medicine for acid indigestion, in cheese making, in leather treatment, and in the treatment of textiles.

(3) *Sodium dihydrogen phospate*, $NaH_2PO_4$, is used as a boiler compound and as a constituent of baking powders.

(4) *Sodium and ammonium phosphates* are used in the treatment of wood and textiles for flame-proofing purposes.

(5) *Calcium phosphate*, $Ca_3(PO_4)_2$, though insoluble in water, is used as a fertilizer. It changes slowly in the soil by the weather process into the soluble dihydrogen-phosphate.

(6) *Calcium dihydrogen phosphate*, $Ca(H_2PO_4)_2$, is used as a fertilizer (constituent of superphosphate). The pure compound is used in baking powders as it improves the ageing properties of bread.

(7) *Calcium monohydrogen phosphate*, $CaHPO_4$, is used as a polishing agent in toothpastes, and as a mineral animal food.

(8) *Glycerophosphates* as well as *sodium and calcium* phosphates are used in medical preparations.

## 18. Pyrophosphoric Acid, $H_4P_2O_7$

**Preparation.** This acid is prepared by heating the orthophosphoric acid to 250°C.

$$2H_3PO_4 \xrightarrow{250^\circ C} H_4P_2O_7 - H_2O\uparrow$$

**Properties and reaction.** (1) Pyrophosphoric acid is a white, crystalline solid, m.p. 61°C. It is a tetrabasic acid but gives only two series of salts such as $Na_2H_2P_2O_7$ and $Na_4P_2O_7$.

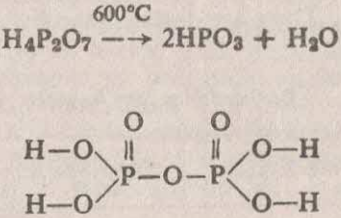
(2) It is soluble in water. In solution it slowly changes into orthophosphoric acid; the change is rapid if the solution is boiled.

$$H_4P_2O_7 + H_2O \rightarrow 2H_3PO_4$$

(3) On strong heating, it loses a molecule of water to yield two molecules of metaphosphoric acid.

$$H_4P_2O_7 \xrightarrow{600^\circ C} 2HPO_3 + H_2O\uparrow$$

**Structure**



## 19. Metaphosphoric Acid, $HPO_3$

**Preparation.** Metaphosphoric acid is formed in solution when phosphorus pentoxide is dissolved in cold water.

$$P_2O_5 + H_2O \rightarrow 2HPO_3$$

It can also be made by heating orthophosphoric acid above 400°C.

$$H_3PO_4 \xrightarrow{\Delta} HPO_3 + H_2O$$

The molten solid solidifies as a vitreous mass and is, therefore, called *glacial phosphoric acid.*

**Properties and Reactions**. Pure metaphosphoric acid is a transparent, glassy, deliquescent solid. Its simplest formula is $HPO_3$; the actual composition of its molecule is expressed by the formula $(HPO_3)_x$, where $x=3$, 4, 5, 6, etc. Metaphosphoric acid is very poisonous.

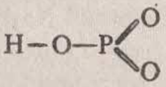
It is readily soluble in water. In aqueous solutions it slowly changes to the ortho acid; the change is rapid on boiling the solution.

$$HPO_3 + H_2O \rightarrow H_3PO_4$$

It is a monobasic acid, and is fairly strong. Its salts, called metaphosphates, often give rise to polymers of the type $(NaPO_3)_n$, where $n$ may be 100—150.

**Uses.** The sodium salt of metaphosphoric acid, sodium hexametaphosphate, $(NaPO_3)_6$, is used for the softening of hard water, for washing purposes and in the treatment of water used in boilers. Its use for these purposes depends on its ability to retain calcium and magnesium salts in solution.

**Structure**



**13-1. Distinction between ortho-, pyro-, and metaphosphates.** All the three kinds of phosphates give a bright yellow precipitate of ammonium phosphomolybdate, $(NH_4)_3PO_4.12MoO_3$, when dissolved in nitric acid and warmed with an excess of ammonium molybdate solution. These are distinguished by the tests summarized in table 12-1.

**Table 12-1** *Distinguishing tests for ortho-, pyro- and metaphosphates*

| *Reagent* | *Orthophosphate* | *Pyrophosphate* | *Metaphosphate* |
|---|---|---|---|
| 1. Neutral $AgNO_3$ soln. | Yellow precipitate, $Ag_3PO_4$ | White, crystalline precipitate, $Ag_4P_2O_7$ | White gelatinous precipitate, $AgPO_3$. |
| 2. Albumen and dil. acetic acid | No effect | No effect | Coagulated |
| 3. Zinc acetate | No effect | White precipitate | No effect |
| 4. Cobaltnitrate | Bluish-violet ppt. | Pink precipitate | No effect |

## 20. Phosphatic Fertilizers

These are substances which are added to the soil to improve its phosphorus content. Important phosphatic fertilizers are :

(1) **Superphosphate of Lime, $Ca(H_2PO_4)_2.H_2O$.** Superphosphate of lime is an important phosphatic fertilizer. It is manufactured by treating calcium phosphate (phosphate rock) with a calculated quantity of concentrated sulphuric acid.

$$\underset{\substack{\text{calcium phosphate}\\ \text{(Insoluble)}}}{Ca_3(PO_4)_2} + 2H_2SO_4 + 5H_2O \rightarrow \underbrace{\underset{\substack{\text{soluble primary}\\ \text{phosphate}}}{Ca(H_2PO_4)_2.H_2O} + 2[\underset{\text{gypsum}}{CaSO_4.2H_2O}]}_{\text{superphosphate of lime}}$$

This reaction is exothermic and is completed in 36—40 hours. The product finally solidifies to a hard mass due to the formation of gypsum. The mass is ground to a fine powder and used as a fertilizer.

(2) **Triple superphosphate.** A more concentrated form of superphosphate called triple superphosphate is produced by the action of phosphoric acid on calcium phosphate (phosphate rock).

$$\underset{\text{phosphate rock}}{Ca_3(PO_4)_2} + 4H_3PO_4 + 3H_2O \rightarrow 3\underset{\text{triple superphosphate}}{[Ca(H_2PO_4)_2.H_2O]}$$

The resulting product contains 42—46% of $P_2O_5$.

(3 **Nitrophosphate.** It is produced by the action of nitric acid on phosphate rock (instead of the sulphuric acid for making superphosphate). The resulting material, called nitrophosphate, supplies both nitrogen and phosphorus to the soil.

(4) **Phosphatic slag or Thomas meal.** It is formed as a slag in the manufacture of steel, and is a mixture of calcium silicate and calcium phosphate. Iron ore (which contains calcium phosphate and sand as impurity) is heated with limestone, coke, and air to produce iron. The phosphorus pentoxide displaced from calcium phosphate reacts with lime (from limestone) to reform calcium phosphate while lime and sand interact to form calcium silicate. The mixture of calcium phosphate and calcium silicate floats atop the molten iron as slag. It is separated, cooled to solidify, and then ground to a fine powder.

$$Ca_3(PO_4)_2 + 3SiO_2 \rightarrow 3CaSiO_3 + P_2O_5$$

$$3CaO + P_2O_5 \rightarrow Ca_3(PO_4)_2$$

$$CaO + SiO_2 \rightarrow CaSiO_3$$

The phosphatic slag contains 14-22% of $P_2O_5$. In the moist soil it slowly decomposes to liberate phosphoric acid for plant growth. Besides, it provides lime which serves to neutralize the acidity in soil.

## Questions

1. (*a*) Write the formula of one compound each having phosphorus in the valence state —3, +3, and +5.

(*b*) Write the formula of a compound containing the $P^{3-}$ ion. Write an equation to show the action of water on this compound.

(*c*) Write the structural formulae of phosphorous acid and metaphosphoric acid.

2. Explain the reason that

*i.* phosphorus forms $PCl_3$ and $PCl_5$ both but nitrogen forms only $NCl_3$;

*ii.* phosphorus froms $PCl_5$ but not $PH_5$,

*iii.* phosphorus vapour on cooling yields white phosphorus and not red phosphorus.

3. Write chemical equations for the following :

(1) A mixture of calcium phosphate, sand, and coke is heated to 1500°C.
(2) White phosphorus is heated with sodium hydroxide solution.
(3) Phosphorus trichloride reacts with water.
(4) Phosphorus pentoxide reacts with water.

4. Show, by means of chemical equations, the action of heat on :

(1) phosphorus pentachloride (3) orthophosphoric acid
(2) phosphorous acid (4) magnesium ammonium phosphate

(5). (*a*) Name three important minerals of phosphorus and write down their chemical formulae.

(*b*) Describe in brief how phosphorus is manufuctured from phosphate rock.

(*c*) How can white phosphorus be changed to red phosphorus and vice versa ?

(*d*) Give one physical method and one chemical method for the separation of red phosphorus from white phosphorus.

(*e*) Explain the reason why red phosphorus is chemically less reactive then white phosphorus.

(*f*) List five main uses of phosphorus.

6. (*a*) How is phosphine prepared in the laboratory ?

(*b*) Compare the reactions of phosphine with those of ammonia.

7. (*a*) Write the structures of phosphorus trioxide and phosphorus pentoxide.

(*b*) How are these oxides prepared ? What happens when these oxides react with water ?

(*c*) Show by means of balanced chemical equations that phosphorus pentoxide is a powerful dehydrating agent.

8. (*a*) How is phosphorous acid obtained ?

(*b*) Give equations to show that it is a reducing agent.

(*c*) Write the structure of phosphorous acid.

9. (*a*) How is orthophosphoric acid prepared ? Give three reactions of the acid along with their equations.

(*b*) Write down equations to show the dissociation of orthophosphoric acid in aqueous solutions.

(*c*) Write the structure of orthophosphoric acid.

(*d*) What changes occur when orthophosphoric acid is heated ? Write the structures of the compounds that are formed.

10. How are the following phosphatic fertilizers produced :

*i*. superphosphate of lime,

*ii*. triple superphosphate,

*iii*. nitrophosphate ?

## Key

1. (*a*) $PH_3$, P = −3; $P_4O_6$, P = +3; $P_4O_{10}$; P = +5

(*b*) $Ca_3P_2$; $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3\uparrow$

2. (*a*) The valence shell in nitrogen, being the second shell ($n=2$), has no *d* orbitals. Hence, it can use only the three unpaired *p* electron of its valevce shell ($2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$) for bonding. So, it cannot form $NCl_5$.

The valence shell ($n=3$) in phosphorus has 2 electrons in the *s* sublevel, 3 unpaired *p* electrons in the *p* sublevel, and five vacant *d* orbitale ($3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$). When the three unpaired *p* electrons are used in reaction with chlorine, $PCl_3$ is formed. However, in its excited state the phorphorus atom will have its *s* electrons unpaired and one of the *s* electrons promoted to a vacant *d* orbital. Thus, in the excited state it has five unpaired electrons and so, forms $PCl_5$.

(*b*) Hydrogen, being weakly electronegative, does not release enough energy in its reaction with phosphorus to unpair the $3s^2$ electrons and promote one of them to a $3d$ orbital. So, it can use only the three unpaired electrons of phosphorus for bonding.

(*c*) Phosphorus vapour is in the highest energy state. On cooling, its changes to the next lower energy state which is white phosphorus. Red phosph - rus is in the lowest energy state.

# 13

# Sulphur

## (An Element of Group VIA)

Sulphur is the second element in Group VIA, preceded by oxygen and followed by selenium (Se), tellurium (Te), and Polonium (Po), the last named being a short-lived radioactive element. The elements in this group are predominantly nonmetallic, although selenium, tellurium, and polonorum do show some metallic properties. This is in keeping with the trend set in the preceding Groups IVA and VA of the nonmetallic characteristics of elements diminishing gradually down the group. The Group VIA being close to the right end of the periodic table, the elements of the group possess high ionization energies which decrease going down the group. An interesting feature of Group VIA elements is that all of them, with the possible exception of polonium, posses allotropic forms.

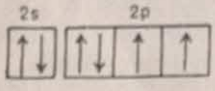
## 1. Position of Sulphur in the Periodic Table

Sulphur follows the first element, oxygen, in Group VIA of the periodic table with the element selenium coming vertically below it. Its horizontal neighbours are phosphorus to the left and chlorine to the right. The position of sulphur in the periodic table is fully justified on the following considerations :

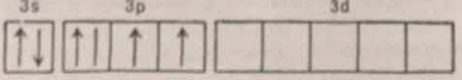
| VA | VIA | VIIA |
|---|---|---|
| N | O | F |
| P | S | Cl |
|  | Se |  |
|  | Te |  |

1. **Electronic configuration.** Sulphur, like the other elements of its group, has six valency electrons ($3s^23p^4$)—one more than in phosphorus ($3s^23p^3$) and one less than in chlorine ($3s^23p^4$).

The electronic configuration of sulphur differs significantly from that of oxygen inasmuch as the valency shell, unlike in oxygen ($2s^22p^4$) possesses vacant *d* orbitals. Hence, these first two elements of Group VIA, though having much in common, exhibit substantial differences also.



*valency shell of oxygen.*

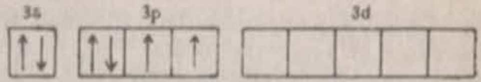


*valency shell of sulphur*

2. **Valency**. The Group VI elements all have the valency shell structure $ns^2np^4$. As such, they tend to attain an inert gas configuration (8 electrons in the outermost shell) by gaining or sharing two electrons. Thus, they all show a valency of −2 with less electronegative elements, *e.g.* in MgO, MgS, etc., and +2 with more electronegative elements, *e.g.*, in $Cl_2O$, $SCl_2$, etc.

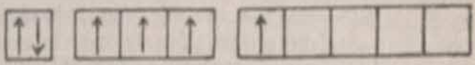
Sulphur (and also Se, Te, and Po) can exhibit higher valencies of +4 and +6 also. This is because in its different excited states sulphur can have four and six unpaired electrons owing to the availability of vacant *d* orbitals.

Sulphur atom
ground state :



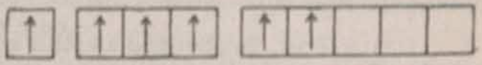
2 unpaired electrons, therefore can form two bonds.

Sulphur atom
excited state :



4 unpaired electrons, therefore can form four bonds.

Sulphur atom further
excited state :



6 unpaired electrons, therefore can form six bonds.

The highest valency of +6 is brought by strongly electronegative elements oxygen and sulphur in $SO_3$ and $SF_6$ respectively.

*Oxygen is never more than divalent* because its valency shell, being the second one, has no vacant *d* orbitals, and it requires too much energy to excite an electron into a higher shell.

3. **Type of bonding**. When oxygen combines with metals, it gains two electrons, consequently most metal oxides are ionic and contain $O^{2-}$ ion. Sulphur is far less electro negative than oxygen and even with the most electropositive elements it does not form the $S^{2-}$ ion. The maximum effective charge on the sulphur atom in sulphides is of the order of −1; *i.e.*, the sulphides are not more than 50% ionic. With elements which are not strongly electropositive, sulphur forms predominantly covalent bonds. Thus compounds such as $H_2S$, $SCl_2$, $SO_2$, etc. all have covalently bonded sulphur.

If we consider the elements P—S—Cl, we find that the ionic character of the binary compounds with metals, *e.g.*, $Mg_3P_2$, MgS, $MgCl_2$ progressively increases in this very order. This is the consequence of the progressive increase in the electronegativity of the elements across a period.

**4. Nonmetallic character.** Sulphur is typically nonmetallic, much more nonmetallic than the elements following it in the group. Horizontally, the nonmetallic character of sulphur is stronger than that of phosphorus, but weaker than that of chlorine. This is reflected in the stability of the hydrides and the nature of the oxides of these elements.

**5. Compounds.** (*i*) *Hydrides.* Sulphur forms the volatile bivalent hydride $H_2S$ corresponding to the hydrides of other elements of the group, *viz.*, $H_2O$, $H_2Se$, $H_2Te$, and $H_2Po$. These hydrides decrease in stability from $H_2O$ te $H_2Po$. $H_2S$ is more acidic than $H_2O$ but less acidic than the other hydrides of the group.

Among the hydrides $PH_3$, $H_2S$, and HCl, the acidic character increases in this very order; $PH_3$ is weakly basic, $H_2S$ is weakly acidic, and HCl is strongly acidic.

(*ii*) *Oxides.* Sulphur forms the oxides $SO_2$ and $SO_3$, both of which are strongly acidic and dissolve in water to give sulphurous acid, $H_2SO_3$, and sulphuric acid, $H_2SO_4$, respectively. Selenium, tellurium, and polonium also forms the dioxides—$SeO_2$. $TeO_2$, and $PoO_2$ which are all solids, unlike $SO_2$ which is a gas under ordinary conditions. Among all these oxides, $SO_2$ is the most strongly acidic and $PoO_2$ the most strongly basic. This is in accordance with the gradual increase in the metallic character going down the group.

(*iii*) *Halides.* Sulphur and all other elements of the group form halides of the type $MX_6$, $MX_4$, $MX_2$, etc. Fluorine brings out the maximum valency of six with S, Se, and Te; and $SF_6$, $SeF_6$, and $TeF_6$ are all formed by direct combination. Among these $SF_6$ is chemically the least reactive. Other halides of sulphur are $SF_4$, $SCl_4$, $SF_2$, $SCl_2$, $S_2F_2$, $S_2Cl_2$, and $S_2Br_2$.

(*iv*) **Compounds of valency −2.** The greatest similarity between sulphur and oxygen is displayed in compounds in which their atoms have a valency of −2, *e.g.*, the oxides and sulphides, and the hydroxides and hydrosulphides. For example, consider these compounds of the elements of the third period :

| | Na | Mg | Al | Si | P | S |
|---|---|---|---|---|---|---|
| Oxide | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ |
| Sulphide | $Na_2S$ | MgS | $Al_2S_3$ | $SiS_2$ | $P_2S_5$ | |
| Hydroxide | NaOH | $Mg(OH)_2$ | $Al(OH)_3$ | $H_4SiO_4$ | $H_3PO_4$ | $H_2SO_4$ |
| Hydrosulphide | NaSH | $Mg(SH)_2$ | $Al(SH)_3$ | $H_4SiS_4$ | $H_3PS_4$ | — |
| Chemical nature | basic | | amphoteric | acidic | | |

It may also be appreciated that the chemical nature of the related oxides, sulphides, hydroxides, etc. changes regularly across a period.

### 4. Sulphur in Nature

Like oxygen, sulphur is also a very common element and occurs in the earth's crust as free element in the form of mineral sulphides and sulphates. Many sulphide minerals are valuable ores, *e.g.* galena, $PbS$; zinc blende, $ZnS$, silver glance, $Ag_2S$, cinnabar, $HgS$, etc. Free sulphur is found in the volcanic regions in Sicily, Japan, South America, Mexico, Greenland, and Iceland. Rich deposits of very pure sulphur exist below the surface of earth in Texas and Louisiana in the U.S.A. In our country, only very small deposits of the element occur in the Kangra district in Himachal Pradesh.

### 5. Extraction of Sulphur

Native sulphur is separated from the rocky impurities (*e.g.*, clay, silica, limestone, etc.) by melting out, usually at the expense of the heat evolved due to the combustion of the sulphur itself. About 30 per cent of the sulphur is used up as fuel in the process.

Over 80 per cent of the world's production of sulphur is mined from the underground deposits in Louisiana and Texas. The mining of sulphur from these deposits was not possible by conventional methods as poisonous gases were present and sulphur was covered up to a height of about 300 metres with mud, gravel, and quick sand which would cause cave-ins. Herman Frasch devised a clever method for the extraction of sulphur from these deposits in which sulphur is pumped to the surface in molten form. The method is known after his name as the Frasch process.

**2-1. The Frasch process**. Three concentric pipes are sunk in a bore hole down to the deposit. Superheated water is passed down the outer pipe, and this melts the sulphur underground. The molten sulphur collects in a pool around the open ends of the pipes. Hot, compressed air (at a pressure of about 35 atmospheres) is blown down the inner pipe. A bubbly froth of molten sulphur, water, and air forms which is forced up the middle pipe (Fig. 13-1). This froth is allowed to flow into immense wooden vats, where the sulphur solidifies upon cooling. The sulphur produced is about 99·5 per cent pure, and for most of its uses needs no purification.

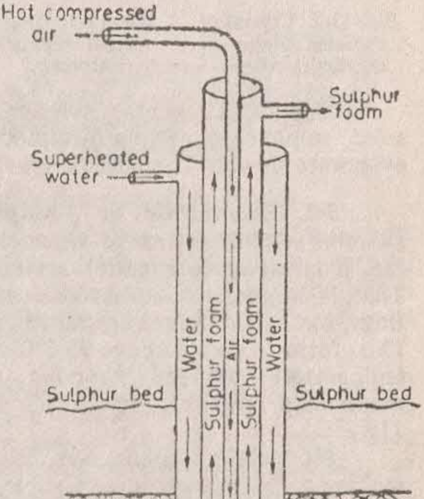


Fig. 13-1. Frasch process for mining sulphur.

## 3. Allotropes of Sulphur

Sulphur exists in several solid and allotropic forms having different arrangements of groups of sulphur atoms. The two crystalline forms are α- or rhombic sulphur and β- or monoclinic sulphur.

**3·1. Rhombic or α- sulphur.** This is the form of sulphur which is stable at ordinary temperature. All other forms of sulphur change to this form upon standing. The crystals of rhombic sulphur belong to the orthorhombic system (Fig. 13-2) and are lemon yellow in colour. The units in the crystal of rhombic sulphur are eight-membered rings of sulphur atoms (Fig. 13-3). The sulphur atoms in the $S_8$ ring are connected to one another by single covalent bonds, each sulphur atom using two of its six valency electrons in forming two covalent bonds (Fig. 13-4). The crystal lattice is molecular in type, the $S_8$ rings being held together in the lattice by relatively weak polar forces. Hence, rhombic sulphur has a rather low melting point.

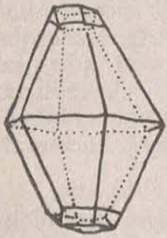


Fig. 13-2. Crystal of rhombic sulphur ; octahedral shape.

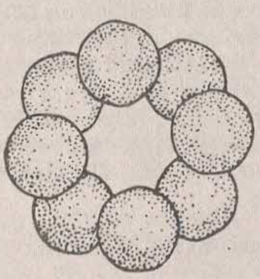


Fig. 13-3. Ring of eight sulphur atoms.

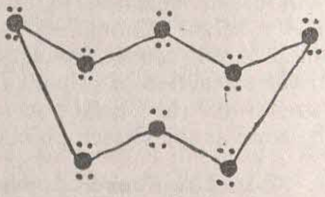


Fig. 13-4. Structure of the $S_8$ molecule of sulphur.

Crystals of rhombic sulphur may be prepared by dissolving solid sulphur in carbon disulphide, and then allowing the solvent to evaporate slowly. The specific gravity of rhombic sulphur is 2·06.

**3·2. Monoclinic or β-sulphur.** At 96°C, the $S_8$ units in rhombic sulphur rearrange themselves to form the monoclinic (prismatic) crystal. (Fig. 13-5). That, is monoclinic sulphur also consists of $S_8$ rings, but in a different crystalline arrangement. This form is stable above 95·6°C, the transition temperature between rhombic sulphur and monoclinic sulphur, up to its melting point 119·2°C.

Monoclinic sulphur can be prepared by melting some sulphur in a crucible, allowing the molten sulphur to cool slowly until a crust just begins to form, and then breaking the crust and pouring out the liquid sulphur. A mass of mono-

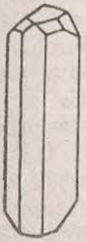


Fig. 13-5. Crystal of monoclinic sulphur.

clinic sulphur will be found lining the surface of the crucible. The specific gravity of monoclinic sulphur is 1·96.

**3-3. λ-Sulphur** (*lambda-sulphur*). Melting of the sulphur results when the binding forces among the $S_8$ molecular units are broken, and the units are free to move. Since the separate $S_8$ units, being spherical, can easily roll over one another, the resulting amber-coloured liquid sulphur flows readily. In this form it is called λ-sulphur.

**3-4. μ-Sulphur** (*mu-sulphur*). At 160°C, the liquid sulphur darkens and becomes more viscous. At 200°C, it becomes dark brown and so viscous that it will not flow out when the container is turned upside down. In this form it is called *mu*-sulphur. It results by the disruption of the $S_8$ ring molecules and the formation of long chains of sulphur atoms $S_\infty$, consisting of several hundreds of thousands of atoms.

As the temperature of lambda sulphur increases, the sulphur atoms acquire enough energy to cause the eight-membered rings to break open. The sulphur atoms on either side of the broken ring are each left with an unshared electron. These sulphur atoms form bonds with similar sulphur atoms from other open rings, producing long chains of $S$ atoms (Fig. 13-6). These chains tangle together, causing the high viscosity of the μ-sulphur. As the number of eight-membered rings of sulphur atoms breaking open increases, the viscosity of the resulting μ-sulphur also increases. The darker colour of μ-sulphur arises from the greater absorption of light by the electrons which formerly completed the ring structure, but which have now become free and move along the chain structure.

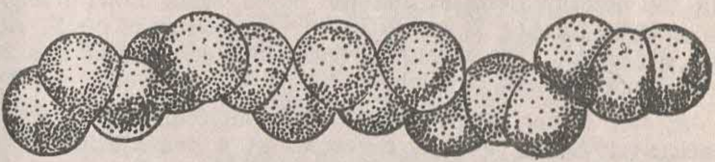


Fig. 13-6. Part of a chain of sulphur atoms in *mu*-sulphur.

**3-5. Plastic sulphur.** If boiling sulphur is poured into cold water, a dark brown rubbery amorphous mass results. This form of the element is called plastic sulphur. It is a supercooled liquid and is insoluble in carbon disulphide, unlike the other two solid forms of sulphur. Its specific gravity is 1·95.

At the boiling point of sulphur, the long tangled $S_\infty$ chains have largely broken down, and are in equilibrium with the resulting $S_8$ rings. On rapid cooling, an amorphous mass is produced which consists of a mixture of ring molecules and chain molecules in an intertwined random state. It is elastic owing to its capacity to revert into a tangled mass of zigzag chains when stretched. However, plastic sulphur soon loses its elasticity, becoming hard and brittle with the $S_8$ ring configuration of the stable rhombic variety.

## 4. Physical Properties of Sulphur

The physical properties of rhombic sulphur, the allotrope of sulphur stable at ordinary temperature, are as follows :

(1) It is a yellow solid, hard and brittle. It forms octahedral crystals which melt at 112·8°C. Its specific gravity is 2·06.

(2) It is almost tasteless and odourless.

(3) It is insoluble in water, sparingly soluble in alcohol and ether, and readily soluble in carbon disulphide and carbon tetrachloride.

(4) It is a poor conductor of heat and electricity.

**4-1. Effect of heat on sulphur.** When sulphur is heated in the absence of air, it undergoes a series of changes. These can be easily observed by heating powdered sulphur in a test tube as in it only a small area of sulphur is exposed so air.

*i.* It melts at 112·8°C to a clear, straw-coloured liquid which flows freely. It is known as *lambda sulphur*, $S\lambda$.

*ii.* At a higher temperature, the straw-coloured liquid rapidly darkens to amber colour and becomes more viscous. About 200°C, it becomes so thick that it does not flow out even on inverting the tube. It is now like thick, dark tar. This liquid form of sulphur is called *mu-sulphur*, $S\mu$.

*iii.* As the boiling point approaches, the chains of sulphur atoms in $\mu$-sulphur break up into smaller groups of atoms. As a result, the viscosity decreases and the liquid again flows freely. It boils at 444°C forming $S_8$ vapour by the vaporization of the $S_8$ rings which still remain. The vapour condenses on a cold surface as a fine, yellow powder (flowers of sulphur).

*iv.* At higher temperatures the $S_8$ molecules progressively dissociate into $S_6$, $S_4$, and $S_2$ molecules as a consequence of the increased molecular motion. As the composition of the molecules alters, the colour of sulphur vapour changes from orange yellow to a straw yellow. About 2000°C, the $S_2$ molecules dissociate into atoms. $S_2$ molecules are paramagnetic and similar in structure to $O_2$ molecules. In all its other states sulphur is diamagnetic.

The changes described above occur in the reverse order on cooling. These may be summarized as given below :

$$\underset{\text{rhombic}}{S} \overset{96^\circ}{\rightleftharpoons} \underset{\text{monoclinic}}{S} \overset{113^\circ}{\rightleftharpoons} \underset{\text{liquid}}{S\lambda} \overset{200^\circ}{\rightleftharpoons} \underset{\text{liquid}}{S\mu} \overset{444^\circ}{\rightleftharpoons} \underset{\text{vapour}}{S_8} \overset{1000^\circ}{\rightleftharpoons} \underset{\text{vapour}}{S_2} \overset{2000^\circ}{\rightleftharpoons} \underset{\text{vapour}}{S}$$

The relative proportion of the two liquid forms of sulphur, $S\lambda$ and $S\mu$, varies with temperature. This accounts for the difference in the properties (*e.g.*, colour and viscosity) of sulphur at different temperatures.

## 5. Reactions of Sulphur

1. **Burning**. When heated to 250°C in air or oxygen, sulphur burns with a pale-blue flame and combines with oxygen to form sulphur dioxide, $SO_2$. A little sulphur trioxide, $SO_3$, is also formed.

$$S + O_2 \rightarrow SO_2$$

$$2S + 3O_2 \rightarrow 2SO_3 \textit{ (in traces)}$$

2. **Combination with nonmetals.** (*a*) Sulphur, combines with hydrogen to form hydrogen sulphide, $H_2S$, when hydrogen is passed through boiling sulphur.

$$H_2 + S \rightarrow H_2S$$

(*b*) When sulphur vapour is passed over red-hot carbon (charcoal), the two elements combine to give carbon disulphide, $CS_2$.

$$C + 2S \rightarrow CS_2 \textit{ (carbon disulphide)}$$

(*c*) On passing chlorine through boiling sulphur. sulphur chloride, $S_2Cl_2$, is obtained as an orange-yellow liquid.

$$2S + Cl_2 \rightarrow S_2Cl_2 \textit{ (sulphur monochloride)}$$

3. **Combination with metals**. Sulphur combines with mercury even at the temperature of liquid air. The two elements readily combine when rubbed together to form mercuric sulphide, HgS.

$$Hg + S \rightarrow HgS \textit{ (mercuric sulphide)}$$

It combines with copper, zinc, iron, etc. on heating to form their sulphides.

$$2Cu + S \rightarrow Cu_2S \textit{ (cuprous sulphide)}$$

$$Fe + S \rightarrow FeS \textit{ (iron sulphide)}$$

4. **With acids**. Sulphur does not react with hydrochloric acid under any conditions. It is unaffected by dilute sulphuric acid and dilute nitric acid. Hot concentrated sulphuric acid oxidises it to sulphur dioxide.

$$\begin{array}{l} H_2SO_4 \rightarrow SO_2 + H_2O + O] \times 2 \\ \underline{S + 2O \rightarrow SO_2 \qquad\qquad\qquad} \\ S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O \end{array}$$

Boiling concentrated nitric acid oxidises it to sulphuric acid.

$$\begin{array}{l} 2HNO_3 \rightarrow 2NO_2 + H_2O + O] \times 3 \\ \underline{S + 3O + H_2O \rightarrow H_2SO_4 \qquad\qquad\qquad} \\ S + 6HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O \end{array}$$

5. **With alkalis**. Sulphur dissolves in hot, concentrated solutions of alkalis, *e.g.*, sodium hydroxide, forming a mixture of alkali sulphide, sulphite, and thiosulphate.

$$\underset{\text{sulphur}}{3S} + \underset{\text{sodium hydroxide}}{6NaOH} \longrightarrow \underset{\text{sodium sulphide}}{2Na_2S} + \underset{\text{sodium sulphite}}{Na_2SO_3} + \underset{\text{water}}{3H_2O}$$

$$Na_2SO_3 + S \rightarrow Na_2S_2O_3 \textit{ (sodium thiosulphate)}$$

Sodium pentasulphide is also formed in very small quantities.

$$Na_2S + 4S \rightarrow Na_2S_5 \text{ (sodium pentasulphide)}$$

6. **With potassium chlorate.** Sulphur forms explosive mixtures with potassium chlorate which detonate when heated or struck.

## 6. Uses of Sulphur

1. *In chemical industry.* The largest single use of sulphur is in the production of *sulphuric acid* by the contact process. Sulphur is burned to *sulphur dioxide*, which is used in bleaching straw and wool. Sulphur is also used in producing *carbon disulphide* (used as an industrial solvent), *phosphorus trisulphide* (used in the match industry), *calcium sulphide* (used for bleaching wood-pulp in the paper industry), *sulphites, thiosulphates, gun-powder* (mixture of sulphur, charcoal, and nitre), etc.

2. *As a bactericide and fungicide.* Owing to its bactericidal and fungicidal properties, sulphur is used in ointments for skin diseases and in sprays for fruit trees (*e.g.*, lime-sulphur spray).

3. *In rubber industry.* Raw rubber is heated with sulphur at a definite temperature for a definite time. This treatment converts the soft sticky mass of rubber into a hard, tough substance, called vulcanized rubber. Articles made of vulcanized rubber retain their shapes.

4. *In medicines.* Colloidal sulphur is used in oral medicines. Many sulphur compounds of metals are used as oral medicines in the *Ayurvedic* system. *Makaradhwaj* (मकरध्वज), made of mercury and sulphur, is a famous *Ayurvedic* tonic.

5. *In the manufacture of sulphur dyes* which are used for dyeing hosiery goods.

## 7. Hydrogen Sulphide, $H_2S$

7.1. **Hydrogen sulphide in nature.** Hydrogen sulphide occurs in volcanic gases and in the waters of sulphur springs. It forms continually as a result of the decay of the proteins in dead animals and plants. This accounts for the strong odour of hydrogen sulphide in the air around cesspools, garbage piles, drainage waters, etc. Especially large quantities of hydrogen sulphide are formed during the rotting of egg albumin. which is the reason for the characteristic odour of rotten eggs.

7.2. **Preparation of hydrogen sulphide.** Hydrogen sulphide can be prepared by the direct union of its elements, *e.g.*, by bubbling hydrogen through molten sulphur. However, the method is not practical because the reaction is reversible and, as it is usually carried out, not more than two per cent of the elements remain combined.

$$H_2 + S \rightleftharpoons H_2S + 5{,}260 \text{ cal.}$$

*Laboratory preparation.* Hydrogen sulphide is prepared in the laboratory by the action of dilute sulphuric acid on iron sulphide.

$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S \uparrow$$

Pieces of iron sulphide are placed in a bottle fitted with a thistle funnel and a delivery tube (Fig. 13-7). Dilute sulphuric acid is poured down the thistle funnel when hydrogen sulphide is evolved with brisk effervescence. The gas is collected by the upward displacement of air.

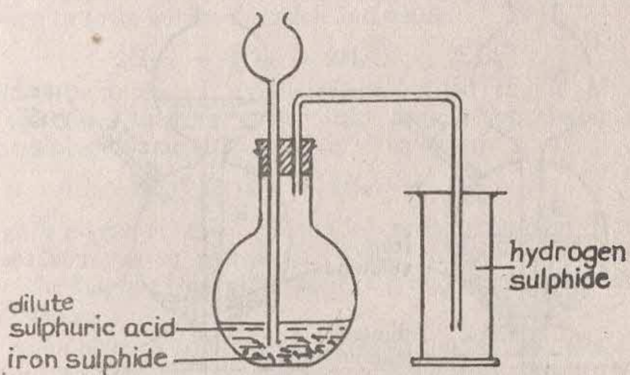


Fig 13-7. Preparation of hydrogen sulphide in laboratory

If required, hydrogen sulphide can be dried by passing it through calcium chloride or phosphorus pentoxide. Concentrated sulphuric acid cannot be used for drying hydrogen sulphide since it reacts with it according to the equation :

$$H_2SO_4 + H_2S \rightarrow 2H_2O + SO_2 \uparrow + S \downarrow$$

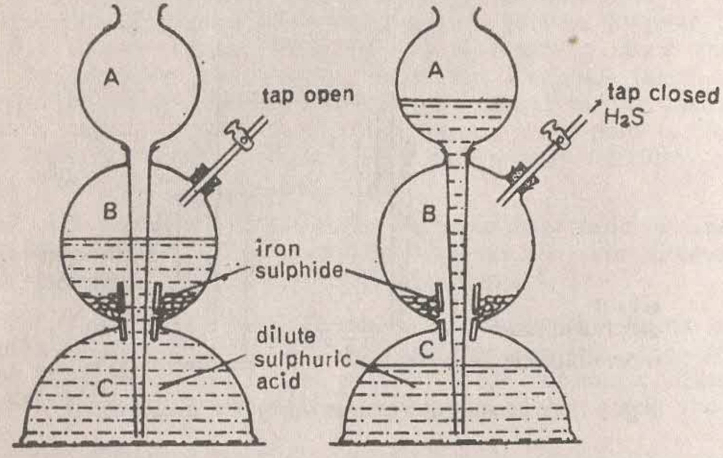
*Pure hydrogen sulphide* is made by heating powdered antimony sulphide, $Sb_2S_3$, with concentrated hydrochloric acid.

$$Sb_2S_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2S \uparrow$$

The gas is washed with water to remove hydrochloric acid, dried over phosphorus pentoxide, and collected by upward displacement of air in dry gas jars.

**7-3. Use of Kipp's apparatus.** Hydrogen sulphide, for intermittent use in qualitative analysis, is generated in Kipp's apparatus (Fig. 13-8). It consists of two detachable parts : the upper part is a bulb (A) with a long stem, and the lower part is made of two bulbs B and C joined together. The stem of A fits air tight into the neck of the bulb B. Pieces of iron sulphide are placed in the bulb B and dilute sulphuric acid is poured in through A until it fills C; reaches B, and covers the iron sulphide. Reaction starts and hydrogen sulphide is liberated. The gas collects in the bulb B above the acid. As more and more of the gas collects, its pressure progressively increases. At a certain stage, the pressure of the gas pushes down the acid from the bulb B into C, and then, through the stem, into A. The reaction now stops as iron sulphide is no longer in contact with the acid.

When the gas collected in B is taken out through the tap, its pressure over the acid falls. This causes the acid to rise up into the bulb B. The reaction once again starts and continues until the acid is again pushed away by the pressure of the accumulated gas.*



(*a*) When the gas is taken out, the acid rises up in the bulb B and more gas is generated.

(*b*) The pressure of the gas collected in the bulb B pushes out the acid and no more gas is generated.

Fig. 13-8. Preparation of hydrogen sulphide in Kipp's apparatus.

**7.4. Physical properties of hydrogen sulphide.** (1) Hydrogen sulphide is a colourless gas with a repulsive, rather sweet smell resembling that of a rotten egg.

(2) It is slightly heavier than air (V.D. of air=14·4; V.D. of hydrogen sulphide=17).

(3) Hydrogen sulphide is fairly soluble in cold water (3 volumes of gas in 1 volume of water) but escapes on warming the solution.

(4) It liquefies when compressed at a low temperature. Liquid hydrogen sulphide boils at —60°C and freezes at −83°C.

(5) It is poisonous in nature. When inhaled in small amounts, it produces severe headache and unconsciousness; larger amounts may cause death.

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*Many other gases may be similarly generated in the Kipp's apparatus for intermittent use, *e.g.*, hydrogen (granulated zinc and dilute sulphuric acid), carbon dioxide (marble pieces and dilute hydrochloric acid), etc.

**7-5. Reactions of hydrogen sulphide.** Important reactions are :

1. *Thermal dissociation.* When heated, hydrogen sulphide begins to dissociate into its elements at 310° ; the dissociation is complete at 1700°C.

$$H_2S \rightleftharpoons H_2 + S$$

2. *Burning.* Hydrogen sulphide is very inflammable and mixed with air, it is explosive. In the air hydrogen sulphide burns with a bluish flame to form sulphur dioxide and water.

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$$

When hydrogen sulphide is ignited in a limited supply of air or when a cold object such as a porcelain dish is introduced into a hydrogen sulphide flame, free sulphur is deposited.

$$2H_2S + O_2 \rightarrow 2H_2O + 2S$$

Advantage is taken of this reaction to recover sulphur from the waste gases from crude petroleum, which contain much hydrogen sulphide. The sulphur thus obtained is an important by-product in the oil industry.

3. *As an acid.* A solution of hydrogen sulphide in water turns blue litmus red and, in general, possesses acidic properties. This acid, often called *hydrosulphuric acid*, is a very weak acid. It ionizes mainly according to the equation

$$H_2S \rightleftharpoons H^+ + HS^-$$

and to a small extent as

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

giving sulphide ions. As such, it is a dibasic acid and neutralizes alkalis to form two series of salts the hydrosulphides and the sulphides.

$$NaOH + H_2S \longrightarrow \underset{\text{sodium hydrogen sulphide}}{NaHS} + H_2O$$

$$2NaOH + H_2S \longrightarrow \underset{\text{sodium sulphide}}{Na_2S} + 2H_2O$$

Most of the more reactive metals will displace hydrogen from hydrogen sulphide, especially at elevated temperatures. For example,

$$Pb + H_2S \rightarrow PbS + H_2 \uparrow$$

$$Sn + H_2S \rightarrow SnS + H_2 \uparrow$$

If silver is placed in hydrogen sulphide solution, it immediately turns black due to the formation of black silver sulphide on its surface. However, the oxygen of the air also takes part in this reaction.

$$4Ag + 2H_2S + O_2 \rightarrow 2Ag_2S + 2H_2O$$

4. *As a reducing agent.* Because the sulphide ion in hydrogen sulphide readily gives up electrons to oxidizing agents to form sulphur atom, hydrogen sulphide is an active reducing agent. It reduces—

*i.* halogens to hydrogen halides,

$$Cl_2 + H_2S \rightarrow 2HCl + S$$
$$Br_2 + H_2S \rightarrow 2HBr + S$$

*ii.* iron (III) salts to iron (II) salts,

$$2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S\downarrow$$

*iii.* sulphur dioxide to sulphur,*

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S\downarrow$$

*iv.* sulphuric acid to sulphur dioxide,

$$H_2SO_4 + H_2S \rightarrow 2H_2O + SO_2 + S\downarrow$$

*v.* nitric acid to nitrogen dioxide,

$$\begin{array}{c} 2HNO_3 \rightarrow H_2O + 2NO_2 + O \\ H_2S + O \rightarrow H_2O + S \\ \hline 2HNO_3 + H_2S \rightarrow 2H_2O + 2NO_2 + S\downarrow \end{array}$$

*vi.* acidified potassium permanganate solutions (pink) to manganese(II) salts (colourless solutions).

$$\begin{array}{c} 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O \\ [H_2S + O \rightarrow H_2O + S] \times 5 \\ \hline 2KMnO_4 + 3H_2SO_4 + 5H_2S \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S \end{array}$$

potassium permanganate (Pink solution) — potassium sulphate, manganese(II) sulphate (Colourless solution)

or, ionically

$$2MnO_4^- + 6H^+ + 5H_2S \rightarrow 2Mn^{2+} + 8H_2O + 5S$$

*vii.* acidified potassium dichromate solution to chromium (III) solutions (solution turned green).

$$\begin{array}{c} K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O \\ [H_2S + O \rightarrow H_2O + S] \times 3 \\ \hline K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S \end{array}$$

potassium dichromate (Orange solution) — potassium sulphate (Colourless), chromium(III) sulphate (Green solution)

Or, ionically

$$Cr_2O_7^{2-} + 8H^+ + 3H_2S \rightarrow 3Cr^{3+} + 7H_2O + 3S$$

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*The deposits of sulphur in volcanic regions may be the result of this reaction since both hydrogen sulphide and sulphur dioxide are present in volcanic gases.

5. *Precipitation of sulphides.* Hydrogen sulphide, when passed through solutions of certain salts, precipitates their sulphides. For example,

$$CuSO_4 + H_2S \rightarrow CuS\downarrow + H_2SO_4$$

$$ZnCl_2 + H_2S \rightarrow ZnS\downarrow + 2HCl$$

Or, in the ionic form,

$$Cu^{2+} + H_2S \rightarrow CuS\downarrow + 2H^+$$

$$Zn^{2+} + H_2S \rightarrow ZnS\downarrow + 2H^+$$

Obviously, a metal sulphide will be precipitated from the solution of its salt if it is not soluble in dilute acids which are formed in such reactions. This is why iron sulphide is not precipitated when hydrogen sulphide is passed through a solution of an iron salt. However if an alkali is previously added to the solution, iron sulphide will be precipitated as the acid formed will be instantaneously neutralized. An even simpler method is to treat the iron salt with a soluble sulphide, say, $Na_2S$, instead of hydrogen sulphide; no acid will be formed at all, and the iron sulphide will be thrown away as a black precipitate.

$$FeSO_4 + Na_2S \rightarrow FeS\downarrow + Na_2SO_4$$

Or, $$Fe^{2+} + Na_2S \rightarrow FeS\downarrow + 2Na^+$$

Advantage is taken of the difference in solubility of sulphides in analytical chemistry for successive precipitation of metals from the solutions of their salts. The metal sulphides fall into three groups :

(*i*) Those which are precipitated from acidic solutions. These are placed in group II of the qualitative analysis. These are

$HgS$, $PbS$, $Bi_2S_3$, $CuS$—Black $Sb_2S_3$—Orange
$CdS$, $As_2S_3$, $SnS_2$ —Yellow $SnS$ —Chocolate brown

(*ii*) Those which are not precipitated in acidic medium but are precipitated in ammoniacal solution in the presence of ammonium chloride. These are placed in group IV of the qualitative analysis. These are—

$ZnS$—White; $MnS$—Buff; $NiS$ and $CoS$—Black

(*iii*) Those which are soluble in water and are not precipitated by $H_2S$, *e.g.*, $Na_2S$, $K_2S$, etc.

**7·6. Tests for hydrogen sulphide.** (1) The gas is colourless with a characteristic smell of rotten eggs.

(2) It produces a black stain on filter paper moistened with lead acetate (due to the formation of lead sulphide).

$$\underset{\text{lead acetate}}{(CH_3.COO)_2Pb} + \underset{\text{hydrogen sulphide}}{H_2S} \longrightarrow \underset{\text{acetic acid}}{2CH_3.COOH} + \underset{\text{lead sulphide}}{PbS\downarrow}$$

(3) It produces a black stain on a silver coin (due to the formation of black silver sulphide).

$$4Ag + 2H_2S + O_2 \rightarrow 2Ag_2S + 2H_2O$$

(4) It produces a beautiful purple colour with an ammoniacal solution of sodium nitroprusside.

**7·7. Uses of hydrogen sulphide.** (1) *As an* analytical reagent in the laboratory in qualitative analysis.

(2) *For the preparation of certain metal sulphides* which are used as pigments in paints and varnishes.

**7·8. Molecular formula of hydrogen sulphide.** Hydrogen sulphide is formed when hydrogen is passed through boiling sulphur. On heating or sparking, it decomposes into hydrogen and sulphur. Thus synthesis as well as analysis shows that *hydrogen sulphide is made up of only hydrogen and sulphur*. Its formula may be determined by either of the following methods :

**Method 1.** A known volume of hydrogen sulphide is enclosed over mercury in an eudiometer tube (Fig. 13-9). Electric sparks are passed through the gas when it decomposes into hydrogen and sulphur. The tube is allowed to cool but the volume of the enclosed gas does not change. This shows that *when hydrogen sulphide decomposes it leaves its own volume of hydrogen.*

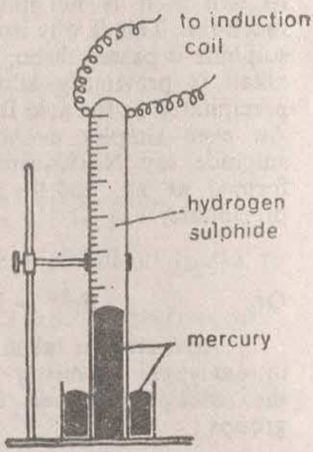

Fig. 13-9. Eudiometer tube.

**Method 2.** A small quantity of tin foil is placed in the bottom of a thumb tube. It is now filled with mercury and its mouth is dipped under mercury in a trough. A small volume of pure and dry hydrogen sulphide is introduced in the tube over mercury (Fig. 13-10). The tin foil is heated when it reacts with hydrogen sulphide liberating its hydrogen and combining with its sulphur to form tin sulphide. The tube is allowed to cool. The level of mercury in the tube remains where it was before heating the tin. Hence, the volume of hydrogen liberated is equal to the volume of hydrogen sulphide. That is, *hydrogen sulphide contains its own volume of hydrogen.*

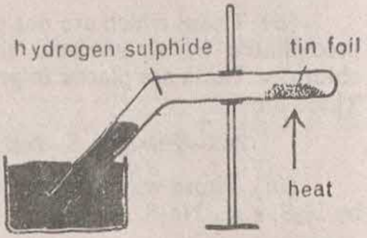

Fig 13.10. Determination of the formula of hydrogen sulphide by decomposing it with heated tin.

Thus,

*1 volume of hydrogen sulphide contains 1 volume of hydrogen.*

∴ *1 molecule of hydrogen sulphide contains 1 molecule of hydrogen.* (*By Avogadro's hypothesis*)

Hence, the molecular formula of hydrogen sulphide is $H_2S_x$.

Its molecular weight from the formula $H_2S_x = 2+32x$.

The vapour density of the gas determined experimentally is 17.

Hence, its molecular weight is $2\times17=34$.

$\therefore \quad 2+32x=34; \quad$ or, $\quad x=1$

Therefore, the molecular formula of hydrogen sulphide is $\mathbf{H_2S}$.

## 8. Sulphides

Sulphur directly combines with a number of less electronegative elements to form binary compounds* called sulphides. The sulphides of metalic elements may be regarded as the salts of hydrosulphuric acid, (hydrogen sulphide), $H_2S$, formed by the replacement of its hydrogen by the metal, *e.g.*, $Na_2S$, ZnS, etc.

**8-1. Preparation of sulphides**. The common methods are :

(*i*) *By heating the metal with sulphur, e.g.*,

$$Fe+S\rightarrow FeS; \qquad Zn+S\rightarrow ZnS$$

(*ii*) *By heating a metal in hydrogen sulphide e.g.*,

$$Sn + H_2S \rightarrow H_2\uparrow + SnS \text{ (\textit{stannous sulphide})}$$

(*iii*) *By passing hydrogen sulphide through the solution of salts.* This results in the precipitation of insoluble sulphides *e.g.*,

$$HgCl_2 + H_2S \rightarrow HgS+2HCl$$

(*iv*) *By neutralising on alkali with hydrogen sulphide, e.g.*

$$2NaOH + H_2S \rightarrow Na_2S + 2H_2O$$

(*v*) *By reducing sulphates with carbon* at high temperatures. For example,

$$BaSO_4 + 4C \xrightarrow{\Delta} BaS + 4CO\uparrow$$

**8-2. General properties of sulphides.** (1) *Solubility.* The sulphides of alkali metals ($Na_2S$, $K_2S$, etc.) are soluble in water; those of alkaline earth metals (CaS, BaS, MgS, etc.) hydrolyse, in water to form soluble hydrosulphides, *e.g.*

$$MgS + H_2S \rightleftharpoons \underset{\text{magnesium hydrosulphide}}{Mg(HS)_2}$$

and those of other common metals are insoluble in water.

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*Only those binary compounds of sulphur are called sulphides in which it is combined with a more electropositive element. Thus, $H_2S$, $Na_2S$, CuS, etc., are all sulphides, but $S_2Cl_2$ is not chlorine sulphide because chlorine is less electropositive than sulphur. This compound is named as sulphur chloride.

(2) *Action of heat.* The sulphides of alkali metals (Na, K, etc.) and of alkaline earth metals (Ca, Sr, Ba) are stable towards heat. Other sulphides decompose on heating in air to give sulphur dioxide and a residue of the metal or its oxide. For example,

$$HgS + O_2 \rightarrow Hg + SO_2 \uparrow$$

$$2CuS + 3O_2 \rightarrow 2\,CuO + 2SO_2 \uparrow$$

In some cases, sulphides are converted into sulphates when heated in excess of air.

$$ZnS + 2O_2 \rightarrow ZnSO_4$$

(3) *Reaction with acids.* Sulphides are decomposed by dilute hydrochloric or sulphuric acid with liberation of hydrogen sulphide.

$$FeS + 2HCl \rightarrow FeCl_2 + H_2S \uparrow$$

With nitric acid, the liberated hydrogen sulphide is oxidized to sulphur.

**8-3. Tests for hydrogen sulphide.** (*1*) *Dilute acid test.* When treated with diluted sulphuric acid, sulphides give out hydrogen sulphide which is recognized by its characteristic smell.

(2) *Sodium nitroprusside test.* An aqueous solution of a sulphide produces a beautiful purple colour with sodium nitroprusside solution. Insoluble sulphides are tested by boiling them with excess of sodium carbonate solution and treating the filtrate (which contains sodium sulphide) with sodium nitropruside solution.

(3) *Silver nitrate or lead acetate test.* An aqueous solution of a soluble sulphide (or the sodium carbonate extract of an insoluble sulphide) gives a black precipitate with silver nitrate or lead acetate.

$$\underset{\substack{\text{sodium}\\ \text{sulphide}}}{Na_2S} + \underset{\substack{\text{silver}\\ \text{nitrate}}}{2AgNO_3} \longrightarrow \underset{\substack{\text{silver sulphide}\\ \text{(black ppt.)}}}{Ag_2S \downarrow} + \underset{\substack{\text{sodium}\\ \text{nitrate}}}{2NaNO_3}$$

$$\underset{\substack{\text{lead}\\ \text{acetate}}}{(CH_3.COO)_2Pb} + \underset{\substack{\text{sodium}\\ \text{sulphide}}}{Na_2S} \longrightarrow \underset{\substack{\text{sodium}\\ \text{acetate}}}{2CH_3.COONa} + \underset{\substack{\text{lead sulphide}\\ \text{(black ppt)}}}{PbS \downarrow}$$

**8-4. Uses of sulphides.** Many natural sulphides are valuable sources of the metals contained in them. Zinc sulphide is one of the most important sources of zinc, and practically all the world's lead is produced from lead sulphide. Mercury sulphide is the only source of mercury while sulphides of iron are a source of sulphur and sulphur dioxide.

Sulphides find wide application in the dye industry. Many sulphides, *e.g.*, zinc sulphide, are used as pigments in paints and varnishes. A mixture of sodium and potassium sulphides with lime is used to remove the hair from skins.

Polysulphides, *e.g.*, sodium polysulphide, $Na_2S_x$ (obtained by shaking $Na_2S$ solution with sulphur and then evaporating the solution) are used in the manufacture of certain kinds of synthetic rubber.

Yellow ammonium sulphide, $(NH_4)_2S_x$, (obtained by passing $H_2S$ through ammonia solution containing excess of sulphur) is used as a reagent in the qualitative analysis for the separation of the sulphides of groups IIA and IIB.

## 9. Sulphur Dioxide, $SO_2$

**9-1. Sulphur dioxide in nature.** Sulphur dioxide is formed in small amounts wherever materials containing sulphur, such as soft coal, coke, or even oil are burned. Hence, traces of sulphur dioxide are found in the air in industrial districts. This pollution is a health hazard because even in very low concentration sulphur dioxide aggravates bronchial trouble. Its presence in air also damages stonework and plant life. Grave concern is being expressed about the damaging effect of the waste gases from the proposed refinery at Mathura (U.P.) on the famous Taj in Agra.

Sulphur dioxide also occurs naturally in volcanic gases, and in some springs of volcanic regions.

**9-2. Preparation of sulphur dioxide.** Sulphur dioxide can be prepared in the laboratory by the following methods :

1. *By heating concentrated sulphuric acid with copper,* when the former is reduced to sulphur dioxide.

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O + SO_2\uparrow$$

2. *By the action of sulphuric acid (or, hydrochloric acid) upon sodium sulphite or sodium hydrogen sulphite.*

$$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + SO_2\uparrow$$
$$NaHSO_3 + H_2SO_4 \rightarrow NaHSO_4 + H_2O + SO_2\uparrow$$

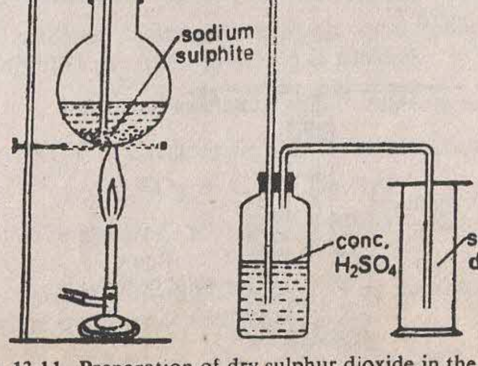


Fig. 13-11. Preparation of dry sulphur dioxide in the laboratory

The gas evolved in the above reactions is collected by upward displacement of air. If required, it may be purified by bubbling through concentrated sulphuric acid (Fig. 13-11).

*Manufacture.* For commercial purposes, sulphur dioxide is made by the following methods :

1. *By burning sulphur in air.*

$$S + O_2 \rightarrow SO_2\uparrow$$

The resulting sulphur dioxide is mixed with nitrogen etc., of the air, but this is not objectionable for most of its applications.

2. *By roasting certain sulphide ores*, as $FeS_2$, ZnS, $Cu_2S$, etc.

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2\uparrow$$

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2\uparrow$$

The roasting of sulphide ores to burn away sulphur as sulphur dioxide is the first step in the metallurgy of these metals. The quantity of sulphur involved in such operations is nearly as much as the total production of free sulphur.

**9-3. Physical properties of sulphur dioxide.** (1) *Colour and odour.* Sulphur dioxide is a colourless gas under ordinary conditions with a pungent, choking odour. Probably, the gas reacts with the water in the nose and throat linings producing irritating $H_2SO_3$.

(2) *Density.* It is about 2·2 times as dense as air (V.D. of air=14·4 of $SO_2$=32).

(3) *Solubility.* Sulphur dioxide is very soluble in water, about 80 volumes dissolving in 1 volume of water at room temperature. Hence, the gas cannot be collected over water.

(4) *Liquefaction.* Sulphur dioxide is readily liquefied to a colourless liquid at room temperature under a pressure of about 2 atmospheres. Liquid sulphur dioxide boils at —10°C and freezes to a snowlike mass at —76°C.

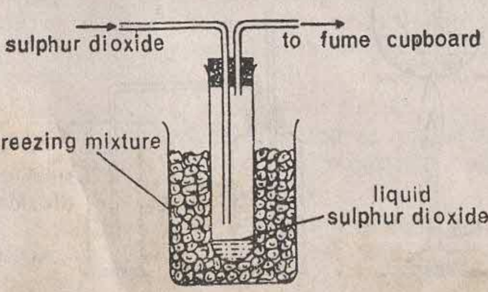


Fig. 13-12. Sulphur dioxide liquefies in a freezing mixture of ice and salt

In the laboratory sulphur dioxide can be liquefied by passing it through a tube immersed in a freezing mixture of ice and salt (Fig. 13-12).

(5) *Solvent properties*. Liquid sulphur dioxide is a good solvent for a wide variety of substances, including many salts. Its electrical conductivity is about twice that of water, and probably it undergoes auto-ionization to a small degree as does water

$$SO_2 + SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-} \ (\textit{autoionization of } SO_2)$$

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \ (\textit{autoionization of } H_2O)$$

The polar character of the $SO_2$ molecules also contributes to its ability to dissolve ionic compounds, giving solutions of high electrical conductivity.

**9-4. Reactions of sulphur dioxide**. The important reactions of sulphur dioxide may be summarized under the following headings :

1. *As an acid anhydride*. Sulphur dioxide behaves as a typical acid anhydride. It combines with water to give a solution of sulphurous acid, $H_2SO_3$.

$$H_2O + SO_2 \rightarrow H_2SO_3$$

It reacts with alkalis giving sulphites (normal salts) and hydrogen sulphites or bisulphites (acidic salts).

$$SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O$$

$$SO_2 + NaOH \rightarrow NaHSO_3$$

Thus sulphur dioxide can be removed from a mixture of non-acidic gases by using concentrated solutions of alkalis.

Sulphur dioxide also directly combine with strongly basic oxides to give sulphites, *e.g.*, calcium sulphite, $CaSO_3$, with CaO :

$$CaO + SO_2 \rightarrow CaSO_3$$

2. *As an oxidizing agent*. Sulphur dioxide acts as an oxidizing agent in many reactions.

i. It oxidizes hydrogen sulphide to sulphur (and is itself reduced to sulphur) provided moisture is present.

$$SO_2 + 2H_2S \rightarrow 2H_2O + 3S$$

ii. At 1000°C it oxidizes carbon to carbon dioxide.

$$SO_2 + C \rightarrow CO_2 + S$$

This reaction is employed for recovering sulphur from industrial flue gases.

iii. It permits burning magnesium to continue burning, oxidizing it into the oxide and sulphide.

$$3Mg + SO_2 \rightarrow 2MgO + MgS$$

Similarly, it oxidizes heated tin, iron, etc., to their oxides and sulphides.

$$3Fe + SO_2 \rightarrow 2FeO + FeS$$

Sulphur dioxide oxidizes burning potassium to potassium sulphite, $K_2SO_3$, and potassium thiosulphate, $K_2S_2O_3$.

$$4K + 3SO_2 \rightarrow K_2SO_3 + K_2S_2O_3$$

iv. In the presence of concentrated hydrochloric acid, it oxidizes iron (II) chloride to iron (III) chloride.

$$4FeCl_2 + 4HCl + SO_2 \rightarrow 4FeCl_3 + 2H_2O + S$$

3. *As a reducing agent.* Sulphur dioxide is a strong reducing agent in aqueous solutions, the essential change being :

$$SO_2 + H_2O + [O] \rightarrow H_2SO_4$$

Or, electronically

$$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H^+ + 2e^-$$

Thus, it reduces

i. halogens to hydrogen halides.

$$SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$$

Since the hydrogen halides are colourless, sulphur dioxide decolorizes solutions of bromine and iodine.

$$SO_2 + 2H_2O + Br_2 \rightarrow H_2SO_4 + 2HBr$$

$$SO_2 + 2H_2O + I_2 \rightarrow H_2SO_4 + 2HI$$

ii. iron (III) salts to iron (II) salts,

$$SO_2 + 2H_2O + 2FeCl_3 \rightarrow 2FeCl_2 + H_2SO_4 + 2HCl$$

iii. acidified potassium permanganate solution (pink) to manganese salts (colourless),

$$\begin{array}{c} 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O \\ SO_2 + H_2O + O \rightarrow H_2SO_4\,] \times 5 \\ \hline \end{array}$$

$$\underbrace{\underset{\text{pot. permanganate}}{2KMnO_4}}_{\text{pink solution}} + 2H_2O + 5SO_2 \rightarrow \underbrace{\underset{\text{pot. sulphate}}{K_2SO_4} + \underset{\text{mang. sulphate}}{2MnSO_4} + 2H_2SO_4}_{\text{colourless solution}}$$

Or, in the ionic form

$$2MnO_4^- + 2H_2O + 5SO_2 \rightarrow 2Mn^{2+} + 4H^+ + 5SO_4^{2-}$$

(*iv*) acidified potassium dichromate solution (orange) to chromium (III) salts (green)

$$\begin{array}{c} K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_2 + 4H_2O + 3O \\ SO_2 + H_2O + O \rightarrow H_2SO_4] \times 3 \\ \hline \end{array}$$

$$\underbrace{\underset{\text{pot. dichromate}}{K_2Cr_2O_7}}_{\text{orange solution}} + H_2SO_4 + 3SO_2 \rightarrow \underset{\text{pot. sulphate}}{K_2SO_4} + \underbrace{\underset{\text{chrom. sulphate}}{Cr_2(SO_4)_3}}_{\text{green solution}} + H_2O$$

Or, in the ionic form

$$Cr_2O_7^{2-} + 2H^+ + 3SO_2 \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$$

4. *Addition reactions.* The normal valency of sulphur is 6. In sulphur dioxide, sulphur is tetravalent, and hence the compound is unsaturated. It therefore gives several addition reactions :

i. It adds on oxygen in the presence of suitable catalysts to give sulphur trioxide.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

ii. It combines with chlorine when the mixture is exposed to sunlight forming sulphuryl chloride, $SO_2Cl_2$.

$$SO_2 + Cl_2 \rightarrow SO_2Cl_2$$

iii. It combines with heated lead dioxide to give lead sulphate.

$$PbO_2 + SO_2 \rightarrow PbSO_4$$

The valency of sulphur in $SO_3$, $SO_2Cl_2$, and $PbSO_4$ is 6.

5. *Bleaching action.* In the presence of moisture, sulphur dioxide bleaches vegetable and animal colouring matter, *e.g.*, litmus, chlorophyll, etc. Presumably the bleaching effect of sulphur dioxide depends upon its reducing action whereby the colouring matter is converted into colourless products. The bleached material is slowly oxidized back into original form on prolonged exposure to light and air, and the colour is restored.

In certain cases, sulphur dioxide combines with the colouring matter to give a colourless addition product. In such a case, the colour may be restored by treating the bleached product with sulphuric acid. The acid liberates sulphur dioxide from the addition product and restores the original colouring matter.

$$\textit{Colouring matter} + SO_2 \underset{H_2SO_4}{\overset{\text{Addition}}{\rightleftharpoons}} \textit{Colourless addition product}$$

The original colour of the bleached article also returns on prolonged exposure to sunshine. In sunshine, the unstable addition product slowly decomposes with the liberation of sulphur dioxide.

6. *With phosphorus pentachloride.* Sulphur dioxide reacts with phosphorus pentachloride to form thionyl chloride, $SOCl_2$, and phosphorus oxychloride, $POCl_3$.

$$SO_2 + PCl_5 \rightarrow SOCl_2 + POCl_3$$

7. *Thermal decomposition.* On strong heating or on passing electric sparks through it, sulphur dioxide decomposes into sulphur and sulphur trioxide

$$3SO_2 \rightarrow S + 2SO_3$$

**9-5. Tests for sulphur dioxide.** (I) It has a characteristic odour of burning sulphur.

(2) It decolorises potassium permanganate solution and bromine solution.

(3) It turns acidified potassium dichromate solution green.

(4) When passed through barium chloride solution containing chlorine (or, bromine) water, it produces a white precipitate of barium sulphate which is insoluble in all acids.

$$BaCl_2 + SO_2 + 2H_2O + Cl_2 \rightarrow BaSO_4\downarrow + 4HCl$$

**9-6. Uses of sulphur dioxide.** Chief uses of sulphur dioxide are :

1. *For making sulphuric acid, sulphites, and hydrogen sulphites.*

2. *As a refrigerent.* Because of its low boiling point (−10°C) and its high heat of vaporization (95 calories per gram), sulphur is used as a refrigerent. However, due to its corrosive nature when traces of moisture are present, it has been largely replaced by ammonia and freon, $CCl_2F_2$.

3. *As a bleaching agent*, especially for silk, wool, straw, and paper which are attacked by chlorine. The bleaching, however, is not permanent and the colour rappears after some time.

4. *As a preservative* for canned fruits such as apricots and prunes, because even in small concentrations it prevents fermentation and the growth of molds.

5. *In petroleum industry.* Liquid sulphur dioxide is used extensively in the petroleum industry for refining kerosene and light oil fractions.

6. *In preparing paper plup.* A solution of calcium hydrogen sulphite, $Ca(HSO_3)_2$, made by reaction of sulphur dioxide and calcium hydroxide, is used in the manufacture of paper pulp from wood. When wood chips are heated in this bisulphite solution, the lignin which binds the cellulose fibres together is dissolved, leaving these fibres, which are then processed into paper.

7. *As a solvent.* Liquid sulphur dioxide is used as a solvent for carrying out certain types of reactions.

**9-7. Formula of sulphur dioxide.** The molecular formula of sulphur dioxide is determined by burning a small piece of sulphur in a confined volume of oxygen. After cooling to original temperature, it is found that there is no change in the volume of the gas. This shows that one volume of oxygen combines with sulphur to produce one volume of sulphur dioxide. That is,

*1 volume of sulphur dioxide contains 1 volume of oxygen.*

*or, 1 molecule of sulphur dioxide contains 1 molecule of oxygen.*
*(By Avogadro's hypothesis)*

*or, 1 molecule of sulphur dioxide contains 2 atoms of oxygen.*
*(∵ oxygen molecule is diatomic.)*

Hence, the molecular formula of sulphur dioxide is $S_xO_2$.

Its molecular weight is, therefore, $32x+32$.

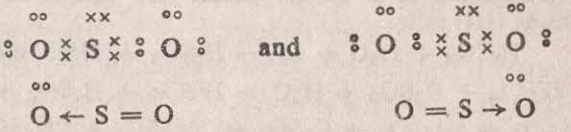
The V.D. of sulphur dioxide is experimentally found to be 32.

Hence, its molecular weight is $2 \times 32 = 64$.

Equating the two values, $32x+32=64$, or, $x=1$.

The molecular formula of sulphur dioxide, therefore, is $SO_2$.

**9.8. The structure of sulphur dioxide molecule.** Sulphur dioxide molecule has a resonating structure involving the two contributing forms whose electronic formulae are given below :



$$\overset{\circ\circ}{\text{O}} \leftarrow \text{S} = \text{O} \qquad \text{O} = \text{S} \rightarrow \overset{\circ\circ}{\text{O}}$$

The shape of the molecular is angular; the angle O—S—O having the value 119·5°.

## 10. Sulphurous Acid, $H_2SO_3$

When sulphur dioxide dissolves in water, it partly reacts with it to give a weakly acidic solution of sulphurous acid, $H_2SO_3$.

$$H_2O + SO_2 \rightleftharpoons H_2SO_3$$

On heating, the equilibrium of this reaction shifts to the left owing to the decreased solubility of sulphur dioxide, and the sulphur dioxide gradually escapes from the solution.

Sulphurous acid, $H_2SO_3$, is a very unstable compound. It is known only in aqueous solutions and cannot be isolated in the anhydrous condition.

Sulphurous acid is a weak, dibasic acid which ionizes in two steps :

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \quad \textit{(primary ionization)}$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-} \quad \textit{(secondary ionization)}$$

The ionization is slight in both stages, but it is much less in the secondary stage than in the primary.

Sulphurous acid forms both normal and acidic salts. Thus, when in excess, it reacts with sodium hydroxide forming sodium hydrogen sulphite, $NaHSO_3$.

$$NaOH + H_2SO_3 \rightarrow NaHSO_3 + H_2O$$

The addition of another mole of sodium hydroxide give the normal sulphite, $Na_2SO_3$.

$$NaOH + NaHSO_3 \rightarrow Na_2SO_3 + H_2O$$

As an acid, sulphurous acid liberates carbon dioxide from carbonates and hydrogen carbonates.

$$Na_2CO_3 + H_2SO_3 \rightarrow Na_2SO_3 + H_2O + CO_2 \uparrow$$

and reacts with magnesium forming magnesium sulphite with the liberation of hydrogen.

$$Mg + H_2SO_3 \rightarrow MgSO_3 + H_2\uparrow$$

Sulphurous acid is rapidly oxidized by the atmospheric oxygen to the more stable sulphuric acid.

$$2H_2SO_3 + O_2 \rightarrow 2H_2SO_4$$

It, therefore, acts as a reducing agent towards strong oxidizing agents in the same way as does sulphur dioxide. Thus, it reduces halogens to corresponding hydrogen halides, iron(III) salts to iron (II) salts, permanganate salts to manganese (II) salts, and dichromates to chromium (III) salts.

$$H_2SO_3 + H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl, \text{ etc.}$$

$$2FeCl_3 + H_2SO_3 + H_2O \rightarrow 2FeCl_2 + H_2SO_4 + 2HCl$$

$$2KMnO_4 + 5H_2SO_3 \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4 + 3H_2O$$

$$K_2Cr_2O_7 + H_2SO_4 + 3H_2SO_3 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O$$

Like sulphur dioxide, sulphurous acid is also a bleaching agent.

Sulphurous acid is tested by the same reactions which are used as tests for sulphur dioxide.

## 11. The Sulphites

The normal salts of sulphurous acid are called sulphites. The soluble sulphites may be prepared by neutralizing alkali solutions with sulphur dioxide. Insoluble sulphites may be obtained by double decomposition. The general properties of the sulphites are summarized below :

(1) *Solubility*. The sulphites of only alkali metals are soluble in water. Their solutions are alkaline due to hydrolysis.

$$\underset{\text{sodium sulphite}}{Na_2SO_3} + \underset{\text{water}}{H_2O} \rightleftharpoons \underset{\text{sodium bisulphite}}{NaHSO_3} + \underset{\text{sodium hydroxide}}{NaOH}$$

(2) *Action of acids*. Dilute sulphuric acid or hydrochloric acid decomposes sulphites with the liberation of sulphur dioxide.

$$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + SO_2\uparrow$$

(3) *Action of heat*. On heating, the soluble sulphites decompose into the corresponding sulphides and sulphates. For example,

$$4Na_2SO_3 \xrightarrow{\Delta} Na_2S + 3Na_2SO_4$$

(4) *With barium chloride*. Soluble sulphites react with barium chloride by way of double decomposition forming a white precipitate of barium sulphite which is soluble in dilute hydrochloric acid.

$$Na_2SO_3 + BaCl_2 \rightarrow BaSO_3\downarrow + 2NaCl$$

$$BaSO_3 + 2HCl \rightarrow BaCl_2 + H_2O + SO_2\uparrow$$

(5) *With silver nitrate*. Soluble sulphites react with silver nitrate to produce a white precipitate of silver sulphite (double decomposition). This precipitate is soluble in dilute nitric acid.

$$Na_2SO_3 + 2AgNO_3 \rightarrow 2NaNO_3 + Ag_2SO_3 \downarrow$$

$$Ag_2SO_3 + 2HNO_3 \rightarrow 2AgNO_3 + H_2O + SO_2 \uparrow$$

(6) *Reducing properties*. Like sulphur dioxide and sulphurous acid, the sulphites are also strong reducing agents. They reduce halogens to corresponding hydr-acids; decolorise acidified potassium permanganate solution; and turn acidified potassium dichromate solution green.

$$Na_2SO_3 + H_2O + I_2 \rightarrow Na_2SO_4 + 2HI$$

These reactions of sulphites serve as tests for their detection.

**11-1. Uses of sulphites.** Sulphites of sodium and potassium are used : (1) in medicines, (2) as antichlor in bleaching by chlorine, (3) as reducing agents, (4) in the preparation of organic chemicals, dyes, etc., (5) for treating rubber latex, and (6) in engraving and lithography.

Solutions of sodium and calcium bisulphite are used in making would pulp from wood.

## 12. Sulphur Trioxide, $SO_3$

**12-1. Preparation of sulphur trioxide.** Sulphur trioxide is formed in minute quantities when sulphur is burned in air or oxygen. However, this method is not suitable for its preparation. It can be prepared by the following methods :

1. *By heating anhydrous iron (II) sulphate.*

$$2FeSO_4 \rightarrow Fe_2O_3 + SO_2 + SO_3$$

2. *By distilling concentrated sulphuric acid with phosphorus pentoxide;* the latter dehydrates sulphuric acid to sulphur trioxide.

$$2H_2SO_4 + P_4O_{10} \rightarrow 2SO_3 \uparrow + 4HPO_3$$

However, these methods, too, are not of much practical value.

3. *By the catalytic oxidation of sulphur dioxide* in the presence of platinized asbestos. This method can be employed in the laboratory, and is also used for making sulphur trioxide in the contact process for the manufacture of sulphuric acid.

$$2SO_2 + O_2 \overset{Pt}{\rightleftharpoons} 2SO_3 + 45{,}200 \text{ cal.}$$

Sulphur dioxide and oxygen are both dried by bubbling through concentrated sulphuric acid. The dry gases are passed over platinised asbestos* heated to 450–500°C in a hard glass tube (Fig. 13-13).

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*Platinized *asbestos* is prepared by soaking asbestos in a solution of ammonium platinichloride $(NH_4)_2PtCl_6$, and then heating is strongly. The salt decomposes leaving fine particles of platinum evenly deposited on the asbestos. In place of platinised asbestos, vanadium pentoxide, $V_2O_5$, may be used as a catalyst.

White fumes of sulphur trioxide are produced by the combination of sulphur dioxide and oxygen. These are led into an ice-cooled receiver fitted with a calcium chloride tube to exclude moisture. Here they condense as white transparent crystals.

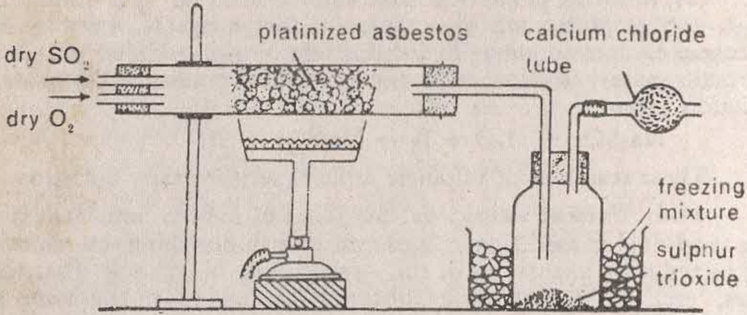


Fig. 13-13. Preparation of sulphur trioxide by the catalytic oxidation of sulphur dioxide.

**12-2. Properties and reactions of sulphur trioxide.** (1) The common form of sulphur trioxide is a silken white, transparent, crystalline solid. It sublimes on heating.

(2) *Thermal dissociation.* When heated, sulphur trioxide dissociates into sulphur dioxide and oxygen; the dissociation being 100 percent at 1000°C.

$$2SO_3 \overset{1000°C}{\rightleftharpoons} 2SO_2 + O_2$$

(3) *Combination with water.* Sulphur trioxide is very deliquescent and for this reason fumes in moist air. The fumes consist of extremely fine droplets of sulphuric acid formed by the combination of sulphur trioxide and water. Sulphur trioxide combines very vigorously and exothermically with water, forming sulphuric acid with a hissing sound.

$$H_2O + SO_3 \rightarrow H_2SO_4$$

It is therefore an *acid anhydroide.*

4. *Acidic nature.* Being an acid anhydride, sulphur trioxide neutralises alkalis to form sulphates and bisulphates.

$$2NaOH + SO_3 \rightarrow Na_2SO_4 + H_2O$$

$$NaOH + SO_3 \rightarrow NaHSO_4$$

It combines with strongly basic oxides *e.g.*, calcium oxide, lead oxide, etc. to form the corresponding sulphates.

$$CaO + SO_3 \rightarrow CaSO_4 ; PbO + SO_3 \rightarrow PbSO_4$$

5. *Combination with sulphuric acid.* Sulphur trioxide dissolves readily in concentrated sulphuric acid forming pyrosulphuric acid, $H_2S_2O_7$, also called "oleum" or "fuming sulphuric acid".

$$H_2SO_4 + SO_3 \rightarrow H_2S_2O_7$$

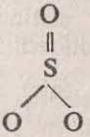
6. *Combination with hydrogen chloride.* Sulphur trioxide combines with hydrogen chloride to give an addition product, chlorosulphonic acid, $Cl.SO_2.OH$.

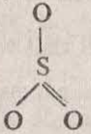
$$SO_3 + HCl \rightarrow Cl.SO_2.OH \text{ (chlorosulphonic acid)}$$

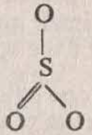
**12-3. Uses of sulphur trioxide.** (1) In the manufacture of sulphuric acid and oleum.

(2) As a drying agent for gases.

**12-4. Structure of sulphur trioxide molecule.** Sulphur trioxide has a resonating structure of three contributing forms given below :







## 13. Sulphuric Acid, $H_2SO_4$

By far the most important and widely used compound of sulphur is sulphuric acid. Next to the manufacture of iron and steel, the manufacture of sulphuric acid is the largest chemical industry in the world.

**13-1. Preparation of sulphuric acid.** (1) *By dissolving sulphur trioxide in water.*

$$H_2O + SO_3 \rightarrow H_2SO_4$$

(2) *By the oxidation of sulphur dioxide in aqueous solution.*

*i.* By atmospheric oxygen :

$$2H_2O + 2SO_2 + O_2 \rightarrow 2H_2SO_4$$

*ii.* By chlorine or bromine :

$$2H_2O + SO_2 + Cl_2 \rightarrow H_2SO_4 + 2HCl$$

*iii.* By hydrogen peroxide :

$$H_2O_2 + SO_2 \rightarrow H_2SO_4$$

**13-2. Manufacture of sulphuric acid.** Most of the commercial sulphuric acid is now produced by the *contact process*, so named because the key step in the process involves contact of sulphur dioxide and oxygen with a catalyst to form sulphur trioxide. In small quantities, sulphuric acid is manufactured by the older *lead chamber process*, which derives its name from the fact that the main reactions are carried out inside large lead-lined chambers.

**1. The contact process for sulphuric acid.** In this process highly purified sulphur dioxide is oxidized to sulphur trioxide by means of air in the presence of a suitable catalyst.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + \textit{heat}$$

The favourable conditions for the maximum yield of sulphur trioxide in this *reversible*, *exothermic* reaction are :

(1) *Low temperature*. The oxidation of sulphur dioxide to trioxide is exothermic and therefore favoured by low temperatures. However, at low temperatures the reaction velocity is too slow to be commercially feasible. Hence, the reaction is carried out at a compromise temperature of about 400°C when about 98 per cent yield of sulphur trioxide is obtained.

(2) *High pressure*. The combination of sulphur dioxide (*2 volumes*) and oxygen (*1 volume*) to form sulphur trioxide (*2 volumes*) proceeds with decrease in volume. Hence, it is favoured by a high pressure. In practice the process is operated at atmospheric pressure because the small improvement in yield hardly justifies the heavy capital cost of the special plant that would be required.

(3) *Excess of oxygen*. An excess of oxygen (air) ensures complete conversion of sulphur dioxide into sulphur trioxide.

(4) *The presence of catalyst*. The most effective catalyst for the conversion of sulphur dioxide to sulphur trioxide is platinum. However, it has been largely replaced by vanadium pentoxide, $V_2O_5$, which is far less susceptible to poisoning and is much less expensive than platinum.

(5) *Purity of the gases*. The reacting gases must be very pure so that the catalyst will work most efficiently.

The various steps in the contact process are :

*i. Production of sulphur dioxide* by burning sulphur (or a sulphide ore) in air in special rotary type burners.

$$S + O_2 \rightarrow SO_2\uparrow$$

$$4FeS_2 + 11O_2 \rightarrow 8SO_2\uparrow + 2Fe_2O_3$$

$$2ZnS + 3O_2 \rightarrow 2SO_2\uparrow + 2ZnO$$

*ii. Purification of gases*. The mixture of sulphur dioxide and air from the burner is purified by passing it successively through a *dust precipitator*, *scrubber* filled with quartz pebbles over which water drips, *drying tower* containing quartz pebbles over which trickles a constant stream of concentrated sulphuric acid, and *arsenic purifier* containing moist iron (III) hydroxide on a number of shelves which absorbs any arsenic oxide (catalytic poison) present in the gases. The gases are then led into a testing box or Tyndall box where they are tested for the complete absence of colloidal solid impurities by making use of Tyndall effect.

In modern plants sulphur dioxide is produced exclusively by burning pure American sulphur in purified air. The resulting gases do not need any further purification. The modern plants, therefore, do not have any purification units.

*iii. Oxidation of sulphur dioxide.* The mixture of purified sulphur dioxide and air is led through a *preheater* into the contact tower, also called the *converter*. It is a cylindrical iron tower containing the catalyst packed in vertical iron pipes (Fig. 13-14). Since the reaction

$$2SO_2 + O_2 \rightarrow 2SO_3$$

is highly exothermic, the catalyst is heated externally only in the beginning to about 400°C. Subsequently, the external heating is discontinued; this temperature being maintained by the heat evolved in the reaction itself.

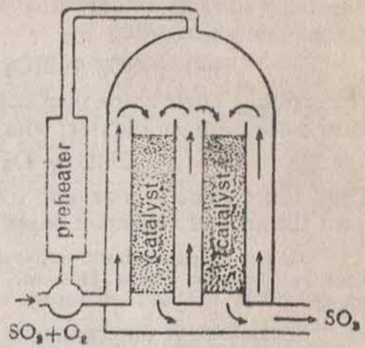


Fig. 13-14. The converter.

*iv. Absorption of sulphur trioxide in concentrated sulphuric acid.* The sulphur trioxide vapour mixed with oxygen and nitrogen enters the absorption tower. The tower is packed with pieces of quartz over which 98 per cent sulphuric acid trickles down from the top. Sulphur trioxide dissolves in sulphuric acid forming oleum or pyrosulphuric acid, $H_2S_2O_7$.

$$H_2SO_4 + SO_3 \rightarrow H_2S_2O_7$$

The waste gas, mainly nitrogen, escapes out the absorption tower.

*v. Addition of water to pyrosulphuric acid.* A calculated quantity of water is added to the pyrosulphuric acid to obtain sulphuric acid of any desired strength. As is clear from the equation,

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

the addition of one mole of water to one mole of pyrosulphuric acid gives two moles of sulphuric acid.

A diagrammatic sketch of the contact process is given in Fig. 13-15.

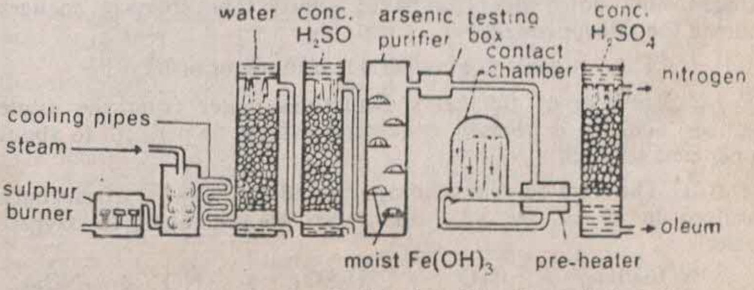


Fig. 13-15. Manufacture of sulphuric acid by the contact process.

**2. The lead chamber process for sulphuric acid.** This process is employed for manufacturing sulphuric acid for such applications which do not require pure or concentrated acid. The process essentially consists in oxidizing sulphur dioxide by nitrogen dioxide, in the presence of water.

$$H_2O + SO_2 + NO_2 \rightarrow H_2SO_4 + NO$$

The resulting nitric oxide then combines with the oxygen of air to form more nitrogen dioxide, which is used again.

$$2NO + O_2 \rightarrow 2NO_2$$

Thus, nitric oxide acts as an *'oxygen carrier'*. It takes up oxygen from the air and delivers it to sulphur dioxide for oxidation.

Concentrated sulphuric acid is used to dissolve the oxides of nitrogen so that they would not escape However, part of these oxides is lost in practice calling for a continuous fresh supply.

**Working.** A diagrammatic sketch of the plant used is given in Fig. 13-16. It consists of the following parts :

(1) *Burners.* Sulphur dioxide is produced by burning sulphur or by roasting iron pyrites in firebrick *burners* in a current of air

$$S + O_2 \rightarrow SO_2$$

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

The burner gases contain about 8 per cent sulphur dioxide, 10 per cent oxygen, and the rest nitrogen.

(2) *Nitre pots.* The hot gases from the burners pass around the nitre pots in which oxides of nitrogen are produced by heating sodium nitrate (nitre) with concentrated sulphuric acid.

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

$$2HNO_3 \rightarrow H_2O + NO + NO_2 + O_2$$

In modern plants, the oxides of nitrogen are supplied by the catalytic oxidation of ammonia.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O;$$

$$2NO + O_2 \rightarrow 2NO_2$$

(3) *Glover tower.* The mixture of sulphur dioxide, air, and the oxides of nitrogen enters the bottom of the *Glover tower* in which dilute chamber acid and nitrated acid containing dissolved oxides of nitrogen flow down over lumps of quartz. The followig changes occur in the Glover tower :

(*i*) The hot gases are cooled down to about 60°C.

(*ii* The heat of the gases evaporates water from the dilute chamber acid. It is thereby concentrated from 65 per cent to about 80 per cent strength.

(*iii*) The nitrated acid decomposes and the oxides of nitrogen dissolved in it are set free. Here, they are used again as 'oxygen-carrier'.

$$\underset{\text{nitrated sulphuric acid}}{2NO.HSO_4} + \underset{\text{water}}{H_2O} \rightarrow \underset{\text{sulphuric acid}}{2H_2SO_4} + \underset{\text{oxides of nitrogen}}{(NO + NO_2)}$$

(*iv*) A part of the sulphur dioxide is oxidized to sulphuric acid.

$$SO_2 + H_2O + NO_2 \rightarrow H_2SO_4 + NO$$

(4) *Lead chambers.* Sulphur dioxide not oxidized in Glover tower, oxides of nitrogen, and excess air enter a set of two or four interconnected lead chambers supported on wooden frames in which steam is blown in from the top. Here sulphuric acid is formed by the changes represented by the following equations :

$$2NO + O_2 \rightarrow 2NO_2$$

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$

$$H_2O + SO_3 \rightarrow H_2SO_4$$

The acid from the chambers collects in a common receiver. This acid is called the 'Chamber acid'. A part of it is pushed by compressed air to the top of the Glover tower and the rest is removed for concentration.

The strength of the chamber acid is kept below 70 per cent by regulated supply of water as stronger acid attacks lead and also absorbs the oxides of nitrogen.

(6) *Gay-Lussac Tower.* The gases escaping from the last chamber contain mainly the oxides of nitrogen and air. These are sent up the Gay-Lussac tower to recover the oxides of nitrogen. It is a cylindrical brick tower lined with sheet lead and is packed with coke. The concentrated sulphuric acid from Glover tower forced by compressed air to the top of Gay-Lussac tower slowly trickles down over coke. It meets the ascending gases and absorbs the oxides of nitrogen forming nitrosyl sulphuric acid (nitrated acid).

$$\underset{\text{sulphuric acid}}{2H_2SO_4} + \underset{\text{oxides of nitrogen}}{(NO + NO_2)} \rightarrow \underset{\text{nitrosyl sulphuric acid}}{2NO.HSO_4} + H_2O$$

The nitrated acid is forced to the top of the Glover tower and allowed to trickle down. Here it gets diluted with the dilute chamber acid and loses the dissolved oxides of nitrogen.

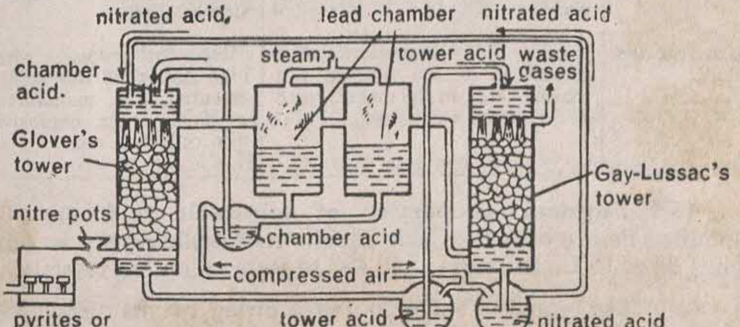


Fig. 13-16. Manufacture of sulphuric acid by the lead chamber process.

(7) *Chimney* (not shown). The waste gas from Gay-Lussac tower escapes through a chimney at one end of the plant. The chimney maintains a draught to keep the gases circulating through the plant.

The acid from the chamber process contains 60 to 70 per cent sulphuric acid and, in contrast to the relatively pure acid produced by the contact process, is impure with lead, iron, and arsenic. It may be concentrated to 77 per cent by heating in lead pans (the dilute sulphuric acid forms a protective coating of lead sulphate which begins to dissolve as lead hydrogen sulphate when the concentration of the acid reaches 77 per cent). Further concentration may be done by evaporation in vessels of silica or duriron (an alloy of iron and silicon) and up to 93 per cent sulphuric acid may be obtained.

### 13-3. Comparison between chamber process and contact process

| *Comparison* | *The Chamber Process* | *The Contact Process* |
|---|---|---|
| 1. Principle | Oxidation of sulphur dioxide by nitrogen dioxide.<br>$SO_2 + NO_2 \rightarrow SO_3 + NO$ | Oxidation of sulphur dioxide by atmospheric oxygen.<br>$2SO_2 + O_2 \rightarrow 2SO_3$ |
| 2. Catalyst | Oxides of nitrogen which are cheap and immune to poisoning. These are produced by heating nitre with concentrated sulphuric acid or by the catalytic oxidation of ammonia. | Platinum catalysts which are costly and highly susceptible to poisoning. Vanadium pentoxide is cheaper and much less susceptible to poisoning but also less effective than platinum catalysts. |
| 3. Purity and strength of the acid | The acid obtained is impure. It is about 78 per cent strong. | Pure acid of any desired concentration (upto 100 per cent) is obtained. |
| 4. Cost of production | Low; because of inexpensive catalyst and ordinary supervision. | High; because of expensive catalyst and expert supervision required. |
| 5. Use of the acid | Used for processes where impurities in the acid do not matter, *e.g.*, in the manufacture of fertilisers, alums, etc. | Used for processes where high purity of the acid is essential, *e.g.*, manufacture of dyes, drugs, explosives, nitrocellulose, etc. |

**13-4. Physical properties of sulphuric acid.** (1) Pure sulphuric acid is a colourless, oily liquid. Its specific gravity is quite high, 1·84 at 15°C. It freezes at 10·4°C to form colourless crystals.

(2) When heated to boiling, it fumes owing to the decomposition of a small portion of the acid into water and sulphur trioxide ($H_2SO_4 \rightarrow H_2O + SO_3$). More sulphur trioxide is lost than water

until the concentration of the acid is reduced to 98·33 per cent. The acid of this concentration boils at 338°C without further change in concentration.

(3) Pure acid is a poor conductor of electricity but in aqueous solutions, it is a good conductor of electricity.

(4) It is soluble in water in all proportions. Much heat is evolved when it dissolves in water. If equal volumes of the acid and water are mixed at ordinary temperature the solution attains a temperature of 120°C. Hence, the acid should be diluted by pouring it slowly into water with continuous stirring. In this way, the heat evolved is distributed unformly. The water must not be added to the concentrated acid as it will be suddenly converted into steam causing dangerous splattering of the acid.

(5) Pure sulphuric acid is *hygroscopic, i.e.*, it absorbs moisture. This is why, the volume of the acid increases after long exposure to moist air.

**13-5. Reaction of sulphuric acid.** (1) *Thermal decomposition.* When dropped on heated pumice stone, sulphuric acid decomposes into water vapour, sulphur dioxide, and oxygen.

$$2H_2SO_4 \rightarrow 2H_2O + 2SO_2 + O_2$$

(2) *Combination with sulphur trioxide.* Concentrated sulphuric acid dissolves sulphur trioxide forming pyrosulphuric acid, $H_2H_2O_7$.

$$H_2SO_4 + SO_3 \rightarrow H_2S_2O_7$$

(3) *As a dehydrating agent.* Concentrated sulphuric acid has great affinity for water. The heat evolved when it dissolves in water is the heat of the reaction between sulphuric acid and water forming the hydrates of the formulae $H_2SO_4.H_2O$, $H_2SO_4.2H_2O$, and $H_2SO_4.4H_2O$. Because of its great affinity for water, concentrated sulphuric acid acts as a powerful dehydrating agent. Thus, it dehydrates

*i.* formic acid, H.COOH, to carbon monoxide, CO;

$$H.COOH + [H_2SO_4] \rightarrow CO\uparrow + [H_2SO_4 + H_2O]$$

*ii.* oxalic acid, $C_2H_2O_4$, to a mixture of carbon monoxide and carbon dioxide;

$$C_2H_2O_4 + [H_2SO_4] \rightarrow CO + CO_2 + [H_2SO_4 + H_2O]$$

*iii.* sugar, $C_{12}H_{22}O_{11}$, to a charred mass of amorphous carbon; and

$$C_{12}H_{22}O_{11} + [H_2SO_4] \rightarrow 12C + [H_2SO_4 + 11H_2O]$$

*iv.* paper and cloth to charred mass of carbon; these substances consist of cellulose, $C_6N_{10}O_5$, which is dehydrated to give amorphous carbon.

$$C_6H_{10}O_5 + [H_2SO_4] \rightarrow 6C + [H_2SO_4 + 5H_2O]$$

Concentrated sulphuric acid spilled on the skin causes painful burns due to dehydration and the accompanying heat, unless the acid is immediately washed off with plenty of water.

(4) *As an acid.* Sulphuric acid almost completely ionizes in solution in two stages as follows :

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$
$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

In dilute solutions sulphuric acid undergoes almost complete primary ionization, the secondary ionization is less complete. Dilute sulphuric acid gives all reactions typical of acids :

*i.* With active metals (above hydrogen):

$$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2\uparrow$$
$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$$

*ii.* Neutralization of alkalis :

$$NaOH + H_2SO_4 \rightarrow NaHSO_4 + H_2O$$
$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$

*iii* With basic oxides :

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$$

*iv.* With carbonates and hydrogen carbonates :

$$MgCO_3 + H_2SO_4 \rightarrow MgSO_4 + H_2O + CO_2\uparrow$$
$$NaHCO_3 + H_2SO_4 \rightarrow NaHSO_4 + H_2O + CO_2\uparrow$$

It may be noted that when concentrated, $H_2SO_4$ is, covalent and metals will not liberate hydrogen from it since $H^+$ ions are not present.

(5) *As a high-boiling acid.* Being a strong acid with a relatively high boiling point, it displaces equally strong acids with lower boiling points when heated with their salts. Hydrochloric acid and nitric acid are thus prepared by heating chlorides and nitrates respectively with concentrated sulphuric acid.

$$NaCl + H_2SO_4 \xrightarrow{\Delta} NaHSO_4 + HCl\uparrow$$
$$KNO_3 + H_2SO_4 \xrightarrow{\Delta} KHSO_4 + HNO_3\uparrow$$

(6) *As an oxidizing agent.* Sulphuric acid acts as an oxidizing agent, especially when concentrated and hot. The hot, concentrated sulphuric acid will oxidize.

*i.* carbon to carbon dioxide and sulphur to sulphur dioxide :

$$C + 2H_2SO_4 \xrightarrow{\Delta} 2H_2O + 2SO_2\uparrow + CO_2\uparrow$$
$$S + 2H_2SO_4 \xrightarrow{\Delta} 2H_2O + 3SO_2\uparrow$$

*ii.* hydrogen bromide to bromine and hydrogen iodide to iodine;

$$2HBr + H_2SO_4 \rightarrow 2H_2O + SO_2 + Br_2$$

$$2HI + H_2SO_4 \rightarrow 2H_2O + SO_2 + I_2$$

*iii.* and metals below hydrogen in the activity series, *e.g.* copper and silver, to their sulphates.

$$Cu + 2H_2SO_4 \xrightarrow{\Delta} CuSO_4 + 2H_2O + SO_2\uparrow$$

$$2Ag + 2H_2SO_4 \xrightarrow{\Delta} Ag_2SO_4 + 2H_2O + SO_2\uparrow$$

In all these reactions sulphuric acid is reduced to sulphur dioxide ($H_2SO_4 \rightarrow H_2O + SO_2 + O$).

(7) *As a sulphonating agent.* Concentrated sulphuric acid reacts with aromatic compounds in such a way that a hydrogen atom is replaced by $-SO_3H$ group. This reaction is called *sulphonation.* Thus, sulphuric acid reacts with benzene and converts it into benzenesulphonic acid.

$$\underset{\text{benzene}}{C_6H_6} + H_2SO_4 \longrightarrow \underset{\text{benzenesulphonic acid}}{C_6H_5.SO_3H} + H_2O$$

(8) *With the salts of lead and barium.* When added to the solutions of the salts of lead and barium sulphuric acid precipitates the corresponding sulphates.

$$Pb^{2+} + H_2SO_4 \rightarrow PbSO_4\downarrow + 2H^+$$

$$Ba^{2+} + H_2SO_4 \rightarrow BaSO_4\downarrow + 2H^+$$

**13-6. Tests for sulphuric acid.** (1) When heated with copper, concentrated sulphuric acid gives off sulphur dioxide which is recognized by its smell and other tests.

(2) When heated with sodium chloride, it liberates hydrogen chloride. This is recognized by the dense white fumes produced in contact with a glass rod moistened with ammonium hydroxide.

(3) It gives a white precipitate of barium sulphate with barium chloride solution and of lead sulphate with lead nitrate solution. These precipitates are insoluble in concentrated hydrochloric or nitric acid.

**13-7. Uses of sulphuric acid.** The major uses are :

(1) *In the manufacture of fertilisers* such as ammonium sulphate, superphosphate of lime, and soluble phosphatic fertilizers.

(2) *In the manufacture of chemicals, e.g.,* hydrochloric acid, nitric acid, phosphoric acid, metal sulphates, ether, etc.

(3) *In the production of dyes, drugs, disinfectants, perfumes, etc. from coal tar* by sulphonation and dehydration reactions.

(4) *In the refining of petroleum* to remove sulphur and tarry compounds from gasoline and kerosene.

(5) *In the manufacture of* ***explosives*** such as nitroglycerine, trinitrotoluene (T.N.T.), picric acid, etc., by acting as a dehydrating agent.

(6) *In metallurgical operations, e.g.*, in the extraction of copper and purification of gold.

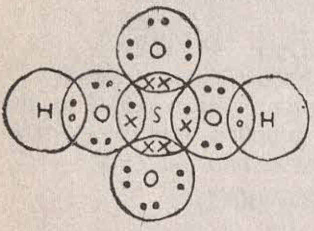
(7) *In the pickling of steel* (*i.e.*, removal of the oxide film) before coating it with tin, zinc, or enamel.

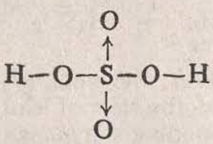
(8) *In lead storage batteries.*

(9) *In the manufacture of* ***miscellaneous*** *articles, e.g.*, paints, pigments, lacquers, plastics, photographic films, cellophane, paper, glue, and other innumerable articles of commerce.

(10) *In the laboratory* as an analytical reagent, dehydrating agent, and drying agent. Oleum is used in sulphonation reactions.

**13-8. Structure of sulphuric acid molecule.** The valence electronic formula and the structural formula of sulphuric acid molecule are given below :





$$\mathrm{H{-}O{-}}\underset{\substack{\downarrow\\ \mathrm{O}}}{\overset{\substack{\mathrm{O}\\ \uparrow}}{\mathrm{S}}}\mathrm{{-}O{-}H}$$

## 14. Sulphates

Being a dibasic acid, sulphuric acid forms both normal salts called the *sulphates*, such as $Na_2SO_4$, and acidic salts called the hydrogen sulphates or *bisulphates*, such as $NaHSO_4$.

The normal sulphates of barium strontium, calcium, and lead are only very slightly soluble in water. These are found in nature as the minerals barytes, $BaSO_4$; celestine, $SrSO_4$; gypsum, $CaSO_4.2H_2O$; and anglesite, $PbSO_4$. These can also be prepared in the laboratory by ionic combination, *e.g.*,

$$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$$

Other sulphates and all bisulphates are soluble in water and, therefore, do not occur in nature. Among the important soluble sulphates are Glauber's salt, $Na_2SO_4$ $10H_2O$; Epsom salt, $MgSO_4.7H_2O$; blue vitriol, $CuSO_4.5H_2O$; white vitriol, $ZnSO_4.7H_2O$, and green vitriol, $FeSO_4.7H_2O$. The soluble sulphates can all be prepared by the action of sulphuric acid on metals, their oxides, hydroxides, carbonates, and other salts of volatile acids.

**14-1. General properties of sulphates.** (*1*) *Solubility in water*. Strontium sulphate and barium sulphate are soluble in water. Sulphates of silver and calcium are only sparingly soluble in water.

(2) *Action of heat.* Sulphates are generally stable towards heat. The sulphates of certain heavy metals decompose on strong heating giving off (*a*) a mixture of sulphur dioxide and oxygen, or (*b*) a mixture of sulphur dioxide and trioxide, or (*c*) only sulphur trioxide. In each case, the residue of the metallic oxide is left behind.

$$2MgSO_4 \rightarrow 2MgO + 2SO_2\uparrow + O_2\uparrow$$

$$2FeSO_4 \rightarrow Fe_2O_3 + SO_2\uparrow + SO_3\uparrow$$

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3\uparrow$$

(3) *Formation of hydrates and double salts.* The sulphates of bivalent metals—magnesium, zinc, cadmium, iron, cobalt, and nickel, crystallise with 7 molecules of water of crystallisation. These sulphates are *isomorphous* with one another. They form double sulphates with the sulphates of alkali metals and with ammonium sulphate. These double sulphates, *e.g.*, $FeSO_4.(NH_4)_2SO_4.6H_2O$, crystallise with six molecules of water and are isomorphous with one another.

The sulphates of trivalent metals—aluminium, chromium, and iron—form double sulphates with the sulphates of alkali metals and with ammonium sulphate. These double sulphates, *e.g.*, $K_2SO_4.Al_2(SO_4)_3.24H_2O$ are called **alums**. They crystallise with 24 molecules of water and are isomorphous with one another. Some other alums are—

$(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$ (*Ammonium alum*)

$K_2SO_4.Cr_2(SO_4)_3.24H_2O$ (*Chrome alum*)

(4) *Reduction.* When strongly heated with charcoal, the metal sulphates are reduced to the corresponding sulphides. For example,

$$Na_2SO_4 + 4C \rightarrow Na_2S + 4CO$$

(5) *Reactions of the sulphate ions.* The soluble sulphates give white precipitate of lead sulphate with lead salts solutions and of barium sulphate with solutions of barium salts. These reactions are due to the sulphate ion, $SO_4^{2-}$.

$$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4\downarrow + 2NaCl$$

or $$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4\downarrow$$

$$Pb(NO_3)_2 + MgSO_4 \rightarrow PbSO_4\downarrow + Mg(NO_3)_2$$

or $$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4\downarrow$$

**14-2. Tests for sulphates.** (1) Aqueous solutions of soluble sulphates give a white precipitate of barium sulphate with barium chloride solution; the precipitate is insoluble in all acids. Insoluble sulphates may be tested by preparing their sodium carbonate extract which contains the soluble sodium sulphate.

(*ii*) The fused mass obtained by fusing a sulphate with sodium carbonate in a charcoal cavity, produces a violet colour with sodium nitroprusside solution. This is due to the formation of sodium sulphate and then its reduction to sodium sulphide.

$$MgSO_4 + Na_2CO_3 \rightarrow MgCO_3 + Na_2SO_4$$

$$Na_2SO_4 + 4C \rightarrow Na_2S + 4CO\uparrow$$

## 15. Thiosulphuric Acid, $H_2S_2O_3$

Sulphites are slowly oxidized to sulphates, and sulphurous acid to sulphuric acid by oxygen. Sulphur plays a role similar to that of oxygen by converting sulphites to thiosulphates. Thus, when a solution of sodium sulphite is boiled with sulphur for a considerable time, it changes to sodium thiosulphate, $Na_2S_2O_3$.

$$Na_2SO_3 + S \xrightarrow{\Delta} Na_2S_2O_3$$

When a solution of sodium thiosulphate is acidified with very dilute sulphuric acid, thiosulphuric acid is formed in solution. It is an unstable compound and slowly decomposes into sulphur, sulphur dioxide, and water.

$$Na_2S_2O_3 + 2HCl \rightarrow H_2S_2O_3 + 2NaCl$$

$$H_2S_2O_3 \rightarrow S + SO_2 + H_2O$$

## 16. Sodium Thiosulphate, $Na_2S_2O_3$

This is the most important salt of thiosulphuric acid. As described earlier it is prepared by boiling sodium sulphite solution with flowers of sulphur until the solution is no longer alkaline.

$$Na_2SO_3 + S \rightarrow Na_2S_2O_3$$

The excess sulphur is filtered off. The filtrate is evaporated to crystallization when crystals of sodium thiosulphate, $Na_2S_2O_3\ 5H_2O$, are deposited on slow cooling.

### 16-1. Properties and reactions of sodium thiosulphate.

(*i*) It is a colourless, efflorescent crystalline substance extremely soluble in water. It has a tendency to form supersaturated solutions.*

(*ii*) *Action of heat*. When heated, sodium thiosulphate decomposes to give sulphur, sulphur dioxide, and hydrogen sulphide.

(*iii*) *Action of acids*. It is decomposed by acids with the evolution of sulphur dioxide and slow precipitation of sulphur.

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + H_2O + S\downarrow + SO_2\uparrow$$

(*iv*) *Action with silver nitrate*. With a very dilute solution of sodium thiosulphate, silver nitrate gives a white precipitate of silver thiosulphate which rapidly changes to yellow, brown, and finally due to the black formation of silver sulphide

$$\underset{\substack{\text{sodium}\\ \text{thiosulphate}}}{Na_2S_2O_3} + \underset{\substack{\text{silver}\\ \text{nitrate}}}{2AgNO_3} \longrightarrow \underset{\substack{\text{silver thio-}\\ \text{sulphate (white)}}}{Ag_2S_2O_3\downarrow} + \underset{\substack{\text{sodium}\\ \text{nitrate}}}{2NaNO_3}$$

$$\underset{\substack{\text{silver thiosulphate}\\ \text{(white)}}}{Ag_2S_2O_3} + H_2O \longrightarrow \underset{\substack{\text{silver sulphide}\\ \text{(black)}}}{Ag_2S\downarrow} + H_2SO_4$$

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*When crystals of sodium thiosulphate are heated in a *clean* test tube, they melt to form a clear solution. If the mouth of the test tube is loosely plugged with cotton to prevent the entry of dust particles, no crystallization occurs on careful cooling. This solution is a supersaturated solution of sodium thiosulphate formed in its own water of crystallization. If a small crystal of sodium thiosulphate is added, crystallization occurs rapidly, and the solution soldiifies.

(*v*) *Action with silver halides.* Solutions of sodium thiosulphate dissolve silver halides forming the soluble complex salt, sodium argento-thiosulphate. Hence, it is used as a fixing solution in photography for dissolving out unchanged silver halide.

$$\underset{\text{silver bromide}}{AgBr} + \underset{\text{sodium thiosulphate}}{2Na_2S_2O_3} \rightarrow \underset{\text{sodium argento-thiosulphate}}{Na_3[Ag(S_2O_3)_2]} + \underset{\text{sodium bromide}}{NaBr}$$

(*vi*) *Action with barium chloride.* In moderately concentrated solutions, sodium thiosulphate interacts with barium chloride to give a white precipitate of barium thiosulphate.

$$Na_2S_2O_3 + BaCl_2 \rightarrow BaS_2O_3 \downarrow + 2NaCl$$

(*vii*) *Action with ferric chloride.* Solutions of sodium thiosulphate give a temporary purple coloration with ferric chloride due to the formation of ferric thiosulphate in a reversible reaction.

$$3Na_2S_2O_3 + 2FeCl_3 \rightleftharpoons Fe_2(S_2O_3)_3 + 6NaCl$$

The purple coloration soon disappears due to the reduction of ferric chloride to ferrous chloride by sodium thiosulphate. This shifts the equilibrium to the left.

$$\begin{array}{c} FeCl_3 \rightarrow FeCl_2 + Cl] \times 2 \\ 2Na_2S_2O_3 + 2Cl \rightarrow Na_2S_4O_6 + 2NaCl \\ \hline 2FeCl_3 + 2Na_2S_2O_3 \rightarrow 2FeCl_2 + Na_2S_4O_6 + 2NaCl \end{array}$$

(*viii*) *Action with halogens.* (*a*) Sodium thiosulphate is oxidized by chlorine or bromine to sodium sulphate.

$$\begin{array}{c} Cl_2 + H_2O \rightarrow 2HCl + O \\ Na_2S_2O_3 + O \rightarrow Na_2SO_4 + S \\ \hline Na_2S_2O_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl + S \downarrow \end{array}$$

(*ix*) Iodine solution oxidizes sodium thiosulphate to sodium tetrathionate, $Na_2S_4O_6$, and is itself decolorized due to the formation of sodium iodide.

$$\underset{\text{sodium thiosulphate}}{2Na_2S_2O_3} + I_2 \longrightarrow \underset{\text{sodium tetrathionate}}{Na_2S_4O_6} + 2NaI$$

**16-2. Uses of sodium thiosulphate.** (1) In *photography* as a fixing solution to dissolve from the plate or film any silver halides which have not been reduced to metallic silver by the developer. When used for this purpose, it is commonly known as 'hypo'.

(2) *In the metallurgy* of gold and silver.

(3) *As an antichlor* for removing excess chlorine in the bleaching of textiles, paper pulp, etc.

(4) *In the laboratory* for the quantitative estimation of iodine solutions.

(5) *In certain medicinal preparations.*

**16-3. Tests for thiosulphates.** (*i*) *Action of acids.* When treated with dilute hydrochloric or sulphuric acid, thiosulphates give off sulphur dioxide and simultaneously depositing pale-yellow particles of sulphur.

(*ii*) *Action of silver nitrate.* When a dilute solution of a thiosulphate is treated with silver nitrate solution, a white precipitate is formed which rapidly changes to yellow, brown, and finally black.

(*iii*) *Action of barium chloride.* Moderately concentrated solutions of a thiosulphate and barium chloride interact to give a white precipitate of barium thiosulphate.

(*iv*) *Action of ferric chloride solution.* Addition of a few drops of ferric chloride solution to a thiosulphate solution produces momentary purple coloration.

(*v*) *Action of iodine solution.* The brown colour of iodine solution is rapidly discharged by a thiosulphate.

(*vi*) *Action of heat.* When a thiosulphate is heated alone, it gives out sulphur dioxide and hydrogen sulphide with the formation of a pale-yellow sublimate of free sulphur.

## 17. Distinctive Tests for Sulphides, Sulphites, Sulphates, and Thiosulphates

| *Reagent* | *Sulphide* | *Sulphite* | *Sulphate* | *Thiosulphate* |
|---|---|---|---|---|
| 1. Dil. acids. | $H_2S$ given off, turns lead acetate paper black. | $SO_2$ given off: turns pot. dichromate green. | No action | $SO_2$ given off, pale yellow ppt. of sulphur formed |
| 2. $BaCl_2$ soln. | No action | White ppt. of $BaSO_3$. soluble in dil $HNO_3$. | White ppt. of $BaSO_4$, insoluble in dil $HNO_3$. | White ppt. of $BaS_2O_3$, soluble in dil. $HNO_3$. |
| 3. $AgNO_3$ soln. | Black ppt. of $Ag_2S$ soluble in $HNO_3$. | White ppt. of $Ag_2SO_3$ soluble in $HNO_3$. | No action | White ppt. of $Ag_2S_2O_3$ changing to yellow, brown, and then black. |
| 4. $FeCl_3$ soln. | Black ppt. | Dark red colour. | No action | Purple coloration |
| 5. Acidified $KMnO_4$ | Decolorized | Decolorized | No action | Decolorized |
| 6. Iodine solution. | No action | Decolorized | No action | Decolorized |

## Questions

1. Explain the reason why—

(1) sulphur shows valency of +2, +4, and +6, while oxygen is never more than divalent,

(2) metal oxides contain the ion $O^{2-}$; metal sulphides are never more than 50% ionic,

(3) solid sulphur has rather a low melting point, and

(4) with rise in temperature, the viscosity of molten sulphur first increases and then decreases.

2. Justify the position of sulphur in the periodic table.

3. (*a*) Arrange the hydrides $PH_3$, $H_2O$, $H_2S$, $H_2Se$, and HCl in the increasing order of acidic nature.

(*b*) Arrange the elements oxygen, sulphur, and selenium in the order of increasing oxidizing strength.

(*c*) Arrange the oxides $P_2O_5$, $SO_3$, and $Cl_2O_7$ in the order of increasing acidic strength.

(*d*) Arrange the elements sulphur, selenium, and tellurium in the order of increasing metallic character.

4. (*a*) The transition temperature between rhombic sulphur and monoclinic sulphur is 95·6°C. What does this statement signify ?

(*b*) What is the unit in the crystals of rhombic sulphur and monoclinic sulphur ? Draw the structure of the unit.

(*c*) Describe the structure of *mu*-sulphur and on the basis of it account for the viscosity and colour of this allotrope.

(*d*) Name the allotrope of sulphur which is insoluble in carbon disulphide. How is it formed ? Describe its structure.

5. Describe the extraction of sulphur by Frasch process.

6. (*a*) Describe and explain the changes which occur when sulphur is heated out of contact with air.

(*b*) Describe the reactions of sulphur with hydrogen, chlorine, sulphuric acid, nitric acid, and sodium hydroxide solution.

(*c*) List the principal uses of sulphur.

7. (*a*) How is hydrogen sulphide usually prepared in the laboratory ? In kipp's apparatus ?

(*b*) Describe the chemical reactions of hydrogen sulphide as an acid, as a reducing agent, and as an analytical reagent in qualitative analysis.

8. (*a*) How is sulphur dioxide usually prepared in the laboratory.

(*b*) Describe the reactions of sulphur dioxide as an acid anhydride, as an oxidizing agent, and as a reducing reagent.

(*c*) Explain the bleaching action of sulphur dioxide.

(*d*) List the main uses of sulphur dioxide.

(*e*) Write down the electronic formula of sulphur dioxide.

9. (*a*) How is sulphur trioxide prepared in the laboratory ?

(*b*) Give four chemical reactions of sulphur trioxide.

(*c*) Write down the structure of sulphur trioxide.

10. (*a*) Discuss the physico-chemical principles underlying the manufacture of sulphuric acid by contact process.

(*b*) Illustrate with suitable examples the reactions of sulphuric acid as a dehydrating agent, as an oxidizing agent, and as a sulphonating agent (give only one example for each role).

(*c*) List the main uses of sulphuric acid.

(*d*) Write down the electronic formula of sulphuric acid.

11. (*a*) How is sodium thiosulphate prepared. Give its reactions with acids, silver nitrate, silver halides, chlorine, iodine and ferric chloride.

(*b*) What are the main uses of sodium thiosulphate ?

(*c*) Give three tests for distinguishing between sulphides, sulphites, sulphates and thiosulphates.

## Key

3. (*a*) $HCl > H_2Se > H_2S > H_2O > PH_3$

(*b*) $O > S > Se$

(*c*) $Cl_2O_7 > SO_3 > P_2O_5$

(*d*) $Te > Se > S$

4. (*a*) The statement signifies that at 95·6°C, the two forms are in a state of equilibrium :

$$S_{\text{rhombic}} \overset{95\cdot6^\circ}{\rightleftharpoons} S_{\text{monoclinic}}$$

When rhombic sulphur is heated to 95·6°C, it is changed, without melting, to the monoclinic form. If the latter, on the other hand, is cooled, the reverse change occurs.

(*b*) The unit in both types of crystals is the same—eight membered ring of sulphur atoms, $S_8$ (structure as shown in Fig. 13-4).

(*d*) The allotrope of sulphur insoluble in carbon disulphide is plastic sulphur.

# 14

# The Transition Elements

## (Iron, Copper, Zinc)

The elements in whose atoms electrons are added to the *d*-sublevel of the penultimate (*i.e.*, outermost but one) shell to fill it from $(n-1)\ d^1$ through $(n-1)\ d^{10}$ configuration are called *d-bloc elements*. These are also called the *transition* elements because they represent sort of transition between the *s*-block elements to their left and the *p*-block elements to their right in the periodic table. Since the *d*-sublevel contains a maximum of 10 electrons, there are ten *d*-bloc or transition elements (atomic numbers 21-30, 39-48, 57 and 72-80) in each of the periods 4, 5, and 6, and one element (number 89 in period 7). In their outermost shell these atoms usually have two electrons, and seldom one. Thus, the electronic configurations of their outer two shells may be represented as $(n-1)\ d^{1-10},\ ns^{1-2}$.

In this chapter we shall study in particular the elements iron, copper, and zinc of the first series of transition elements (numbered 21-30). These elements are not only among the most common and familiar metals, but are also of much practical significance.

## 1. Iron, Copper, and Zinc in the Periodic Table

The position of these elements may be discussed under the following headings :

1. **Electronic configuration.** The elements iron, copper, and zinc belong to the first series of transition elements. This series consists of ten successive elements in the fourth period, from scandium to zinc inclusive, in which the number of electrons in the 3*d* sublevel increases almost regularly from eight to eighteen*. (Table 14-1). Except the elements chromium and copper, all others in the series have 2 electrons in their outermost 4*s* level.

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*The two exceptions are Cr and Cu, where one of the $4s^2$ electrons moves into the 3*d* sublevel, because of the additional stability when the *d* orbitals are exactly half filled or completely filled (See rule 4 governing the build up of atoms, Chap. 1, Sec. 15, page 29.

**Table 14-1** *Electronic configuration of the transition elements of first series*

| *Element* | *Symbol* | *At. No.* | *Electronic configuration* |
|---|---|---|---|
| 1. Scandium | Sc | 21 | $1s^2, 2s^22p^6, 3s^23p^63d^1, 4s^2$ |
| 2. Titanium | Ti | 22 | $1s^2, 2s^22p^6, 3s^23p^63d^2, 4s^2$ |
| 3. Vanadium | V | 23 | $1s^2, 2s^22p^6, 3s^23p^63d^3, 4s^2$ |
| 4. Chromium | Cr | 24 | $1s^2, 2s^22p^6, 3s^23p^63d^5, 4s^1$ |
| 5. Manganese | Mn | 25 | $1s^2, 2s^22p^6, 3s^23p^63d^5, 4s^2$ |
| 6. **Iron** | Fe | 26 | $1s^2, 2s^22p^6, 3s^23p^63d^6, 4s^2$ |
| 7. Cobalt | CO | 27 | $1s^2, 2s^22p^6, 3s^23p^63d^7, 4s^2$ |
| 8. Nickel | Ni | 28 | $1s^2, 2s^22p^6, 3s^23p^63d^8, 4s^2$ |
| 9. **Copper** | Cu | 29 | $1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^1$ |
| 10. **Zinc** | Zn | 30 | $1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^2$ |

2. **Similarities in properties**. In general, the transition elements have an $ns^2$ configuration in the outermost energy level, while the penultimate shell of electrons is expanding. Owing to the identical outer electron configuration, the transition elements show horizontal similarities in physical and chemical properties in contrast to the elements of the *s*- and *p*-blocks. Like the other groups of elements, they show vertical group similarities also. It may be noted that zinc, which has a stable $d^{10}$ configuration in the penultimate shell, shows significant differences from the other elements of the first transition series.

3. **Size**. Atoms of the transition elements are smaller than those of the Group IA or IIA elements in the same horizontal row or period. This is partly because the nuclear charge increases across the period and partly because the orbital electrons are added to the penultimate *d* level rather than to the outer shell of the atom. Thus, the transition elements of the first series have smaller atoms than the preceding *s*-block elements potassium and calcium.

4. **Metallic behaviour**. Transition elements are all hard, lustrous metals, and are good conductors of electricity. For this reason, they are usually called *transition metals*. Since their atoms are smaller, they have higher densities than the metals of the *s*- and *p*-blocks. Their melting and boiling points are generally very high. Zinc is a notable exception because the *d* block is complete in it.

5. **Alloy formation**. Transition metals are ductile and form alloys with other metals. Since they are nearly the same atomic size, they can replace one another in crystal lattices to give solid solutions and smooth alloys.

6. **Variable valency**. Transition metals exhibit variable valency. Many of the elements show a wide range of valencies and the valency changes in units of one, *e.g.*, $Fe^{2+}$ and $Fe^{3+}$, $Cu^+$ and $Cu^{2+}$,

etc. The variable valency of transition metals is due to the fact that the difference in energy between the 4*s* and 3*d* orbitals is very small and, therefore, electrons from both of these orbitals may be involved in bonding. Thus, a transition metal will lose its two 4*s* electrons to form doubly charged positive ion, $M^{2+}$, and exhibit a valency of +2. However, only a small amount of energy is needed to remove its 3*d* electrons. So, in the presence of oxidizing agents, it may lose a 3*d* electron in addition to the two 4*s* electrons to form $M^{3+}$ ion, and exhibit a valency of +3. For example, iron (2,8,14,2) forms $Fe^{2+}$ ion (2,8,14) by the loss of the two 4*s* electrons, and $Fe^{3+}$ ion by the further loss of one 3*d* electron so that the $Fe^{3+}$ ion has the electron configuration 2,8,13.

Titanium, vanadium, chromium, and manganese exert higher valencies by involving one or more electrons from the penultimate shell for covalent bonding, in addition to the outermost electrons. For example, manganese (2,8,13,2) can form covalent bonds using the two 4*s* electrons as well as from one to five of the 3*d* electrons resulting in heptavalent manganese (2,8,18,4) in the oxide $Mn_2O_7$ and in the permanganate ion, $MnO_4^-$.

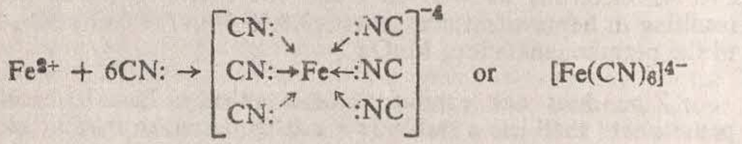
Zinc does not exhibit variable valency. This is because its penultimate shell has a stable $3d^{10}$ configuration, so that 3*d* electrons cannot be involved for bonding.

**7. Type of bonding.** The transition metals can lose up to three electrons to form positive ions, *e.g.*, $M^+$, $M^{2+}$, and $M^{3+}$, but the higher the number of electrons involved in bonding, the more covalent the compound is. That is, the lower valent states are ionic and the higher valent states covalent. Thus, the transition metals may form either ionic or covalent bonds depending on the conditions. In this respect, they are transitional between the *s*-block elements (elements of Groups IA and IIA) which typically form ionic compounds and the *p*-block elements which are largely covalent.

**8. Formation of coloured compounds.** Ionic and covalent compounds of transition metals usually have characteristic colours. This contrasts with the compounds of the *s*- and *p*-block elements which are almost always white. The explanation lies in the fact that in the compounds of the transition metals, electrons are readily promoted from $(n\text{-}1)d$ to *ns* orbitals. This is especially true if there are unpaired electrons, in which case the absorption of some particular colour of visible light provides the right amount of energy to cause this. This absorption of light causes a particular colour to appear. Hydrated cupric ions, $Cu^{2+}$, for example, absorb energy in the red end of the spectrum and transmit or reflect the blue. Solutions of $Fe^{2+}$ ions have green and of $Fe^{3+}$ ions have yellow colour for similar reasons. Cuprous compounds and zinc compounds are white because $Cu^+$ (2,8,18) and Zn (2,8,18) have no unpaired *d* electrons. The energy to unpair *d* electrons and to promote them to a higher energy level is much greater, and is not provided by light in the visible spectrum.

**9. Catalytic activity**. Many transition metals and their compounds are highly active as catalysts. This is due either to the transition metals forming unstable intermediate compounds as a result of variable valency or to their providing a suitable surface for reaction. Some common examples are the use of iron as catalyst in the synthesis of ammonia, of copper in dehydrogenations and in the manufacture of $(CH_3)_2SiCl_2$ for silicones, of nickel in numerous reduction processes, and of $FeSO_4$ and $H_2O_2$ (Fenton's reagent) for oxidizing alcohols to aldehydes.

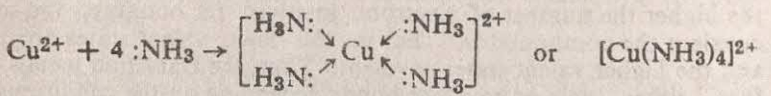
**10. Complex ion formation.** This is one of the most notable feature of the transition metals. In forming complex ions, the simple ions of transition metals share electron pairs on other ions or neutral molecules which are thereby attached to them through coordinate bonds. Thus, iron forms the complex ferrocyanide ion, $[Fe(CN)_6]^{4-}$, by the coordination of $Fe^{2+}$ ion with six cyanide ions, each of which carries a lone pair of electrons on the nitrogen atom.



$$Fe^{2+} + 6CN: \rightarrow \left[\begin{array}{c} CN:\searrow \quad \swarrow :NC \\ CN:\rightarrow Fe \leftarrow :NC \\ CN:\nearrow \quad \nwarrow :NC \end{array}\right]^{-4} \quad \text{or} \quad [Fe(CN)_6]^{4-}$$

ferrocyanide ion

Copper forms tetrammine copper (II) ion, $[Cu(NH_3)_4]^{2+}$, by the coordination of $Cu^{2+}$ ion with four ammonia molecules.



$$Cu^{2+} + 4 :NH_3 \rightarrow \left[\begin{array}{c} H_3N:\searrow \quad \swarrow :NH_3 \\ Cu \\ H_3N:\nearrow \quad \nwarrow :NH_3 \end{array}\right]^{2+} \quad \text{or} \quad [Cu(NH_3)_4]^{2+}$$

tetrammine copper (II) ion

**11. Paramagnetism**. The elements of the first transition series from chromium to nickel inclusive are paramagnetic, *i.e.*, they are attracted by a magnet. Paramagnetism results from unpaired electron spins in the atom. An electron in an atom spins about its axis. Being a charged particle, the spinning electron behaves like a small magnet, with north and south poles. The two paired electrons in an orbital spin in opposite directions, thus cancelling their magnetic effects, because their north and south poles are opposed. On the other hand, atoms with unpaired electrons have an unbalanced magnetic field, and are paramagnetic. The greater the number of unpaired electrons in an atom, the stronger is its paramagnetism.

Iron, cobalt, and nickel display an extreme form of paramagnetism, commonly referred to as *ferromagnetism* because of the unusual extent to which it is possessed by iron. Ferromagnetism is the tendency to be attracted to a magnetic field, and to retain the magnetism after the field has been removed. That is, ferromagnetic substances may become permanently magnetized whereas paramagnetism is shown only in the presence of an applied magnetic field. The ferromagnetism in iron, cobalt, and nickel arises from just the right spacing between the atoms in their crystal lattices so that the unpaired electrons from adjacent atoms cannot overlap to cancel their spins.

## I. IRON

### 2. Historical Background

Iron was known at least as early as 6000 B.C. Ancient Hindus were experts in the extraction of iron from its ores, tempering of steel, and applied processes. They possessed a thorough knowledge of the various processes for the preservation of iron. Ashoka's pillar at Delhi, which was constructed from high class malleable iron in 319 A.D., and stainless steel joints in the temple of Puri speak eloquently of the great skill of the ancient Hindus in this field. In contrast, until the 14th century, iron was so scarce in England that the iron vessels in the kitchen of Edward III were counted among the valuables. The blast furnace for the smelting of iron was introduced in Germany, about 1350 A.D. and in England about 1500 A.D.

### 3. Iron in Nature

Iron ranks second in abundance among the metals (aluminium is first) and fourth among all elements in the earth's crust of which it constitutes nearly 5 per cent by weight. In all probabilities, the core of the earth may be composed of iron. Iron is also present as silicates in clays and soils, and in all living matter, being essential for the production of chlorophyll in plants, and of hemoglobin in blood. In the earth's crust, iron occurs only in the form of various compounds, e.g., oxides, sulphides, carbonates, and silicates. The important ores of iron are : **hematite** or **red iron ore**, $Fe_2O_3$; **limonite** or **brown iron ore**, $Fe_2O_3.3H_2O$; and **magnetite** or **lodestone**, $Fe_3O_4$. *Siderite* or *spathic iron ore*, $FeCO_3$, is a brownish white mineral which is not much valued as an ore of iron.

*Iron pyrites* or just *pyrites*, $FeS_2$, is an abundant iron mineral which, due to high sulphur content, is of little importance as an iron ore. It is, however, an important raw material for the manufacture of sulphuric acid. Owing to its beautiful yellow colour and metallic lustre, this mineral is also known as 'fool's gold'.

### 4. Extraction of Iron

Iron is extracted from its oxide ores* by reduction with carbon at high temperatures in blast furnaces. A blast furnace (Fig. 14-1) is a conical structure, about 25 metres high, made of a steel shell, lined with a layer of fire-resistant brick. The upper two-thirds of the furnace flares out downward to provide proper flow of the charge; the lower one-third narrows down as the materials melt and occupy less space. Pipes or '*tuyeres*' (pronounced *tweeyair*) through which a blast of air preheated to 700-800°C is blown into the furnace open in its lower portion. A little below the tuyeres are two tap-holes, the upper one for the discharge of molten iron and the lower one for the discharge of molten slag. These are kept plugged up with clay except when the molten material is being discharged.

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*Carbonate ores are converted into iron (II) oxide by roasting in excess of air.

$$4FeCO_3 + O_2 \xrightarrow{\Delta} 2Fe_2O_3 + 4CO_2 \uparrow$$

The charge of ore, coke, and flux (limestone for ores containing sand, and sand for ores containing limestone)* is fed into the furnace through the opening at the top. The opening has two successive bell shaped valves, called *airlocks*, one of which remains closed while the other is open. Thus the hot gases cannot escape during charging. As the charge melts, or is burned in the lower regions of the furnace, the stock column gradually sinks leaving room for additional charge at the top. The operation of the blast furnace is thus a continuous process.

The molten metallic iron and the molten slag drip to the bottom of the blast furnace. Here, the lighter slag floats on top of the molten iron and shields it from being oxidized by the incoming air. As they accumulate, the molten slag and the iron are tapped separately through the respective holes

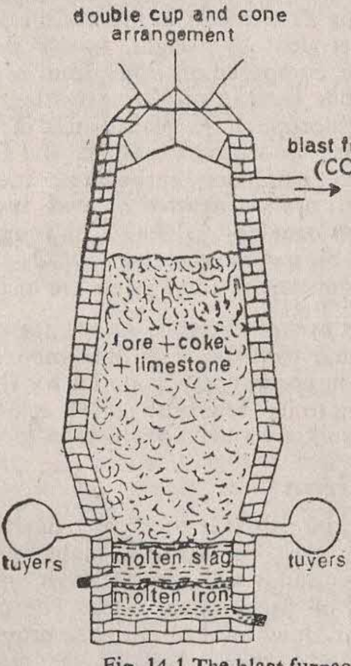

Fig. 14-1 The blast furnace.

**4-1. Chemical reactions within the blast furnace.** The chemical reactions occurring in the blast furnace and the temperatures at various heights are shown in Fig. 14-2.

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*In either case the limestone dissociates to give calcium oxide which combines with the sand to produce the fusible slag of calcium silicate, ($CaO + SiO_2 \rightarrow CaSiO_3$). If no flux is added, the rocky matter in the ore (sand or limestone) will clog the furnace because its melting point is much higher than the temperature in the furnace.

(*i*) In the *lower region* of the tuyeres, the coke is oxidized to carbon dioxide with the liberation of much heat, so that the temperature reaches up to 1400°-1500°C or more at the bottom.

$$C + O_2 \rightarrow CO_2 + 97{,}000 \text{ cal.}$$

(*ii*) In the *middle region*, three reactions take place :

(*a*) The carbon dioxide passing upward through the overlying layer of white-hot coke, is reduced to carbon monoxide.

$$CO_2 + C \rightarrow 2CO - 39{,}000 \text{ cal.}$$

(*b*) The limestone (added as flux or present as an impurity in the ore) dissociates into calcium oxide and carbon dioxide.

$$CaCO_3 \rightarrow CaO + CO_2 - 43{,}250 \text{ cal.}$$

Both of these reactions being endothermic, the temperature in this zone sharply drops to 700–950°C.

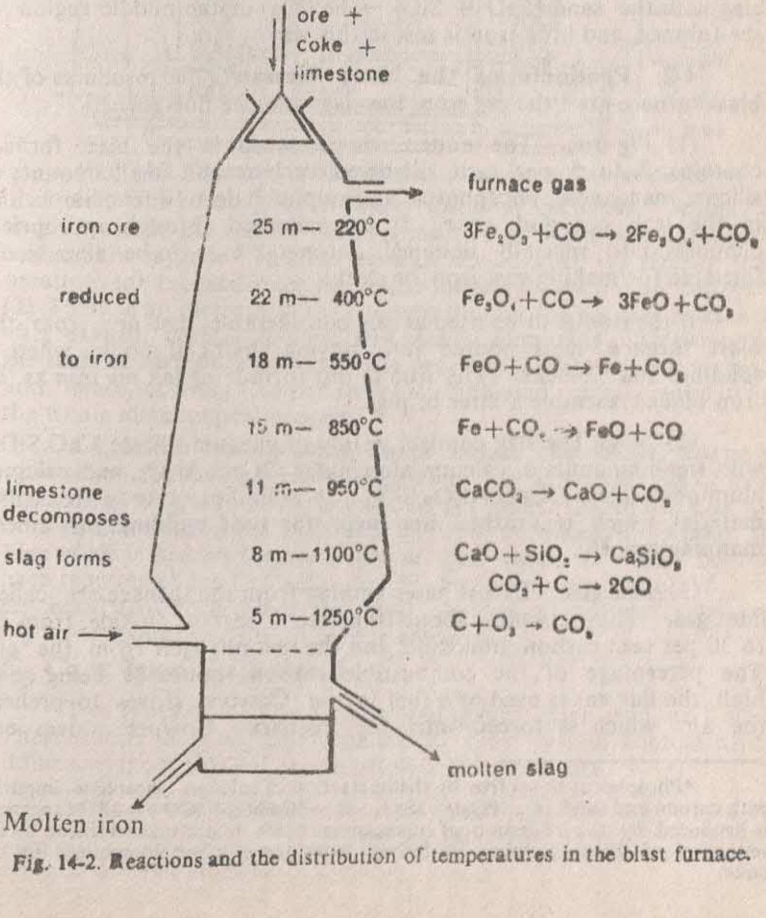
ore +
coke +
limestone
furnace gas
iron ore
reduced
to iron
25 m— 220°C
22 m— 400°C
18 m— 550°C
15 m— 850°C
11 m— 950°C
8 m—1100°C
5 m—1250°C
$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$
$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$
$FeO + CO \rightarrow Fe + CO_2$
$Fe + CO_2 \rightarrow FeO + CO$
$CaCO_3 \rightarrow CaO + CO_2$
$CaO + SiO_2 \rightarrow CaSiO_3$
$CO_2 + C \rightarrow 2CO$
$C + O_2 \rightarrow CO_2$
limestone decomposes
slag forms
hot air
molten slag
Molten iron

Fig. 14-2. Reactions and the distribution of temperatures in the blast furnace.

(*c*) The calcium oxide combines with silica to produce calcium silicate, the fusible slag.

$$CaO + SiO_2 \rightarrow CaSiO_3$$

(*iii*) In the *upper region*, the ore is reduced to iron by the carbon monoxide in several steps represented by the following equations.

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$$
$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$
$$FeO + CO \rightarrow Fe + CO_2$$

These reduction reactions can be summarized as a single reversible reaction as follows :

$$Fe_2O_3 + 3CO \rightleftharpoons 2Fe + 3CO_2$$

The presence of excess of carbon monoxide keeps the equilibrium shifted to the right. The iron oxide, FeO, is reduced before it can slag with the sand ($FeO + SiO_2 \rightarrow FeSiO_3$) in the middle region of the furance, and little iron is lost in this way.

**4.2. Products of the blast furnace.** The products of the blast furnace are : the pig iron, the slag, and the flue gas.

(1) *Pig iron.* The molten iron produced in the blast furnace contains 2 to 5 per cent dissolved carbon and small amounts of silicon, manganese, phosphorus, and sulphur* derived from impurities in the iron ore and coke. It is conducted through appropriate channels into specially designed hot-metal cars to be taken to the furnaces for making cast iron or steel.

If the iron is to be used at any considerable distance from the blast furnace, it is poured into moving chains of moulds where it solidifies into blocks. The iron in this form is called *pig iron* as the iron blocks resemble a litter of pigs.

(2) *Slag.* The slag consists mainly of calcium silicate, $CaO.SiO_2$, with small amounts of calcium aluminates, $2CaO.Al_2O_3$, and calcium aluminosilicates, $3CaO.Al_2O_3.SiO_2$. It solidifies into a rock-like material which is crushed and used for road building, for cement manufacture, etc.

(3) *Flue gas.* Excess gases coming from the furnace are called flue gas. They contain about 10 per cent carbon dioxide, from 20 to 30 per cent carbon monoxide, and the rest nitrogen from the air. The percentage of the combustible carbon monoxide being quite high, the flue gas is used as a fuel in the Cowper stoves to preheat the air which is forced into the furnace. Cowper stoves are

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*Phosphorus is set free by the interaction of calcium phosphate impurity with carbon and sand, $Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 3CaSiO_3 + 5CO\uparrow + 2P$. Manganese is produced by the reduction of manganese oxide impurity, and silicon by the reduction of silica. Sulphur is derived from the sulphur compounds in the coke.

cylindrical towers almost as tall as the blast furnace itself. These are built of firebrick and have vertical channels inside. Each furnace is connected to two or four Cowper stoves. The blast furnace gases, after passage through a dust extractor, enter the stove and burn in it, heating the walls of the channels to redness. At the same time air is blown into the blast furnace through the other stove already heated up in a similar manner. After sometime the air blast is turned into the first stove, and the blast furnace gases burned in the second one (Fig. 14-3).

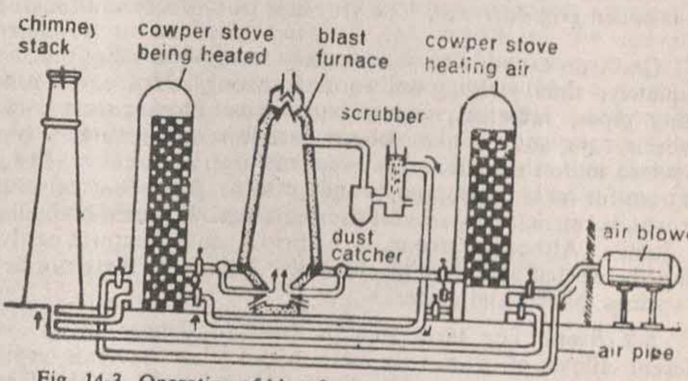

Fig. 14-3. Operation of blast furnace connected to Cowper stoves.

**4-3. Use of oxygen in blast furnace process.** Instead of an air blast, 80 per cent of which is inactive nitrogen, some furnaces utilize pure oxygen. This has several advantages : (1) Higher temperatures are reached since no heat is wasted in heating up nitrogen. (2) There is an increase in the concentration of the gaseous reactants, *viz.*, oxygen, carbon, dioxide, and carbon monoxide. This steps up the rates of various reactions. The necessity for heating the air blast and, hence, of using Cowper stoves is eliminated, greatly simplifying the whole metallurgical process.

**4-4. Some interesting facts about the blast furnace operation.** (1) A single blast furnace may produce 1500 tons of iron, 500 tons of slag, and 2000 tons of flue gas daily. (2) About one ton of coke is consumed for each ton of iron produced. (3) About six tons of air is needed for every ton of iron made. A large blast furnace requires about 13,50,000 dm$^3$ of hot air every minute for the air blast. (4) Once fired, the blast operates continuously day and night for several years until repairs are needed.

## 5. Cast Iron and Steel

Two types of iron is used in industry* : cast iron and steel. These forms of iron differ mainly in their carbon content which influences their physical properties in a great measure.

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**Wrought iron*, the purest commercial form of iron, containing only 0·1 to 0·25 per cent of carbon and less than 0·5 per cent of all other impurities put together, is now largely replaced by mild steel (Sec. 14-8), which matches wrought iron in all desirable properties, yet is cheaper than it.

**5-1. Cast Iron.** When pig iron is remelted with scrap iron in a furnace and recooled in moulds, it is called cast iron. The rusty oxides in the scrap help oxidize carbon, the amount of which is reduced to about 2 per cent. When cooling is done rapidly, white crystalline cast iron is formed. It contains most of the carbon chemically combined with the iron as iron carbide, $Fe_3C$. The product is called *white cast iron.* It is brittle, hard, and resistant to wear. When the molten pig iron is cooled slowly, most of the carbon crystallises as black graphite. The product has, therefore, a grey colour and is called *grey cast iron.* The grey cast iron is soft and tough.

Cast iron expands on solidification in moulds, filling all details completely, thus yielding well-formed castings. Hence, it is used for casting pipes, radiators, automobile engine blocks, stoves, weights flywheels, toys, and the like, where hardness and resistance to wear are prized more than strength. Since cast iron does not readily rust, it is used for making lamp posts and gutters. More extensive use of cast iron is restricted by several shortcomings. It is neither malleable, nor ductile. Although strong, it is brittle and fractures easily. It cannot be welded and is unmachinable. It cannot therefore be used for springs, plates, and girders.

**5-2. Steel.** The term steel is used to denote many widely different alloys of iron with carbon and other elements, especially manganese, silicon, and phosphorus. Most steels contain from 0·1 to 1 per cent carbon. and varying amounts of other elements. Steels are made by removing the impurities from molten pig iron by oxidation and then adding known quantities of carbon and other elements to produce an alloy of desired composition and uses.

## 6. Manufacture of Steel

Three processes are used chiefly for the production of steel : the *Bessemer process*, the *open hearth process*, and the *L.D. process*, steels of high quality for special purposes are made by the *electric-furnace process.*

**6-1. The Bessemer process.** This process is accomplished in a *converter*, an egg-shaped steel vessel lined with firebrick and large enough to hold 15 to 20 tons of the charge. It has a double bottom enclosing an air space. This air space leads to one of the supporting arms of the converter. The upper part of the air space is perforated with small holes through which air is blown during operation. The converter is mounted on pivots which allow it to be tipped back and forth for loading and pouring (Fig. 14-4). For working low-phosphorus pig irons, the converter is lined with silica bricks. Owing to the acidic nature of silica, the process is then called the *acid Bessemer process.* For working high-phosphorus pig irons, the converter is lined with calcined dolomite (CaO.MgO). Owing to the basic nature of this refractory material, the process is then called the *basic Bessemer process.*

*Acid Bessemer process.* Molten pig iron direct from the blast furnace is introduced into the converter by turning it horizontal. A blast of cold air is blown through the charge as the converter is tipped upright again, the inrush of air holding up the metal through the holes. Although a blast of cold air is used, the heat developed by the oxidation of carbon, manganese, silicon, and other impurities raises the temperature and makes iron even hotter than it was in the beginning. The resulting oxides of manganese and silicon react with each other to form manganese silicate ($MnO+SiO_2 \rightarrow MnSiO_3$), which rises to the surface as slag. The carbon monoxide, formed by the oxidation of carbon, burns at the mouth of the converter with roaring yellow flames. When the flames die down (a sign that oxidation is complete), an iron alloy containing carbon and manganese (ferromanganese) is added to deoxidize the steel* and to leave required amounts of these elements in excess. The air is again blown through for a minute to mix the ingradients. The slag is then skimmed off and the molten steel poured out first into a ladle, and then into moulds where it solidifies into ingots.

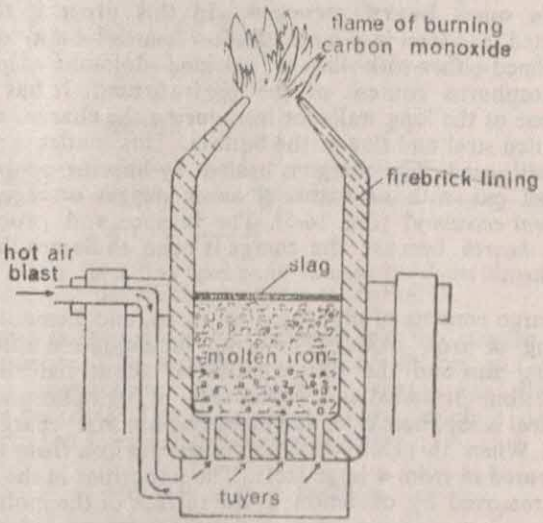

Fig. 14-4. The Bessemer converter

*Basic Bessember Process.* In this process, **the lining of the converter is made of calcined dolomite (CaO.MgO). Quicklime (CaO)** is also added as a flux during blowing **to convert the phosphorus** pentoxide and silica formed by the **oxidation of phosphorus and** silicon (impurities) respectively into **phosphate and silicate slag.**

$$MgO + SiO_2 \rightarrow MgSiO_3$$
$$CaO + SiO_2 \rightarrow CaSiO_3$$
$$3CaO + P_2O_5 \rightarrow Ca_3(PO_4)_2$$

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*The manganese unites with the oxygen left in the product from the blast of air; other metals may be added to produce a steel of the desired properties.

The slag is poured off before adding the ferromanganese. This *basic slag or Thomas slag*, as it is called, is ground to a fine powder and used as a phosphate fertilizer.

Acid Bessemer process is unsuitable for high-phosphorus irons because phosphorus pentoxide, being an acidic oxide, cannot be removed with the 'acid' lining of the converter, which acts as a flux towards the basic oxides of manganese and iron.

The Bessemer process is inexpensive and quick, requiring only 15-20 minutes for a batch of 25 tons of pig iron. However, the lack of control over the composition does not permit the production of 'tailor-made' steels for specific applications. Furthermore, a considerable amount of iron is lost due to the intensive oxidation that occurs.

Bessemer steel is a low grade, but inexpensive product. It finds use in making pipes, wire, hardware, and steel frameworks for bridges and buildings.

6-2. **The open hearth process.** In this process, the pig iron is converted into steel in a large shallow hearth* built of steel plates. It is lined either with silica or calcined dolomite depending upon the phosphorus content of the pig iron used. It has several doors along one of the long walls for introducing the charge, and an outlet for molten steel and slag at the bottom. This outlet is plugged with clay until used. The charge is heated by burning a mixture of preheated fuel gas with an excess of air or oxygen on *regenerative principle of heat economy*† (Fig. 14-5). The furnace and process are named *open hearth* because the charge is open to flames that keep the mass molten.

The charge consists of pig iron, steel scrap, and hematite (iron ore consisting of iron oxide). The scrap, including old automobile bodies, boilers, cans and the like constitutes about half the total charge. Limestone is added as a flux in case of high phosphorus pig irons. The steel scrap, hematite, and limestone are first charged into the furnace. When this charge melts, molten pig iron from the blast furnace is poured in from a large ladle. The impurities in the molten charge are removed by oxidation, at the surface of the molten mass

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*It is about 12 m long, 5 m wide, and slopping to a depth of about 0·6 m in the centre. It can hold up to 300 tons of the charge.

†The furnace (Fig. 14-5) is connected at either end with asystem of two chambers filled with checkerwork firebrick. The gas and air are fed through the chambers at one end (say, air through chamber I by pipe 1; gas through chamber II by pipes 2 and 3). The air and gas mix under the roof and burn to produce intensely hot flames which are deflected down across the charge. The hot products of combustion pass out through the two chambers at the other end. When these chambers become hot, the flow of air and gas is reversed by turning the valves 5 and 6 into the positions indicated by dotted lines. The air and gas become hot as they pass through the chambers just heated. The process thus operates efficiently by conserving the heat of the waste gases which, after being cooled, escape through pipe 4 into the chimney.

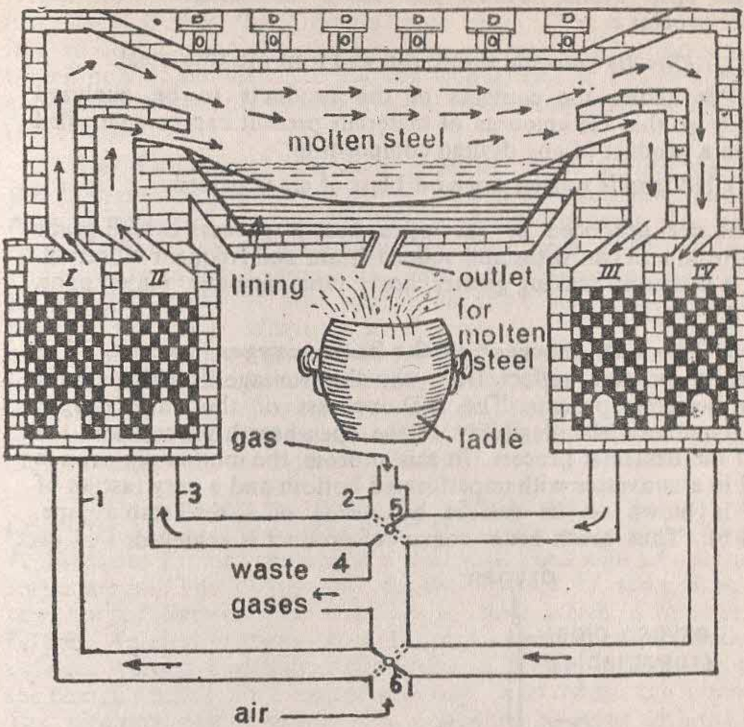

Fig. 14-5. The open hearth furnace; the doors for introducing the charge are marked D.

by the oxygen in the air and on the inside by the oxygen contained in the hematite. The resulting oxides of silicon and manganese (impurities) interact to form slag of manganese silicate while phosphorus pentoxide formed combines with calcium oxide (from limestone flux) to form calcium phosphate slag.

$$MnO + SiO_2 \rightarrow MnSiO_3$$

$$P_4O_{10} + 6CaO \rightarrow 2Ca_3(PO_4)_2$$

$$SiO_2 + CaO \rightarrow CaSiO_3$$

Carbon is oxidized to carbon monoxide by the hematite, while any sulphur present is oxidized to sulphur dioxide. Both of these products escape as gases. About 8-10 hours are required to oxidize most of the carbon. At intervals, samples of the metal are removed for testing, the oxidation being continued until the desired composition is obtained. Carefully controlled amounts of carbon and alloying metals are then added to produce steel of the desired type. The charge is then tapped into a huge ladle. Here a little aluminium is added to the molten steel to remove dissolved gases. The slag overflows into another ladle (not shown in the figure).

The open hearth process has many advantages over the Bessemer process :

(1) It directly converts scrap iron and iron ore into steel.

(2) It allows the contents of the products to be analyzed frequently so that the amounts of materials present can be controlled to obtain a product of any desired composition.

(3) No iron is wasted since no blast of air is passed.

The steel produced by the open hearth process is high-grade and uniform, and can withstand sudden strain and frequent vibration. Hence, it is used in making girders, heavy rails, armour plate, guns, etc.

**6-3. The L.D. process* or the basic oxygen process.** The open-hearth process suffers from the disadvantage of being slower than the Bessemer process. The L.D. process or the *basic oxygen process* combines the flexibility of the open-hearth process with the speed of the Bessemer process. In this process, the molten pig iron is charged in a converter with unperforated bottom and a very fast jet of oxygen is blown on its surface by means of a retractable pipe. (Fig. 14-6). Thus much better control of product is achieved.

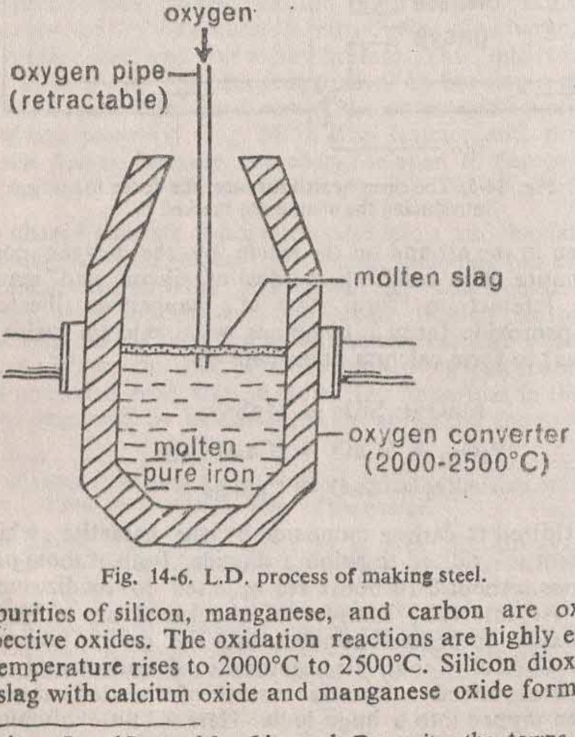

Fig. 14-6. L.D. process of making steel.

Impurities of silicon, manganese, and carbon are oxidized to their respective oxides. The oxidation reactions are highly exothermic and the temperature rises to 2000°C to 2500°C. Silicon dioxide forms $CaSiO_3$ slag with calcium oxide and manganese oxide forms $MnSiO_3$

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*The letter L and D stand for Litz and Donawitz, the towns in Austria, where this process was developed.

slag with silica which float on the surface of molten iron. Purified iron, being denser than impure iron, sinks to the bottom while the impure iron, rises to the surface. The process is a very quick one, taking only 45 minutes in a 100-ton converter. In quality the steels are equivalent to open-hearth steels of the same grade, and are free from nitrides.

**6-4. The electric furnace process**. High quality steel and the high-melting alloy steels containing nickel, chromium, vanadium, molybdenum, etc., are manufactured in electric furnaces. The electric furnaces have several advantages : (*i*) The temperature can be controlled within a few degrees. (*ii*) Temperature as high as 3000°C can be attained which is not possible in any other furnace, making it possible to smelt refractory alloy steels. (*iii*) Since heat is not produced by burning gases, the introduction of extraneous impurities is avoided and a finished product free from blow holes is obtained. (*iv*) The losses of alloying elements are lower than in any other furnaces, and steels containing the heat-resistant metals, *e.g.*, tungsten, molybdenum, etc., can be easily produced.

The electric furnace used in the manufacture of steels are of two types : (*i*) *direct arc furnaces* and (*ii*) *high-frequency induction furnaces.* A direct arc furnace consists of a steel shell lined with a basic refractory material. The charge may consist entirely of scrap iron and steel, or of Bessemer or open-hearth steel which is to be refined further. An electric arc is struck between two carbon electrodes or between carbon electrodes and the charge. The heat of the arc melts the charge which is then treated with oxygen to oxidize the impurities. The resulting oxides are readily converted into slag with the basic lining. The metals to be alloyed are added as elements or as alloys of iron. If necessary, ferrosilicon alloys are added to remove dissolved oxygen. When the process is complete, the liquid steel is poured into moulds by tipping the entire vessel. "Electric steel" may be rolled and forged. It is used in casting frames for motors, pipes, valves, tools, etc. Nearly all steel used in airplanes is electric steel.

High-frequency induction furnaces are essentially melting furnaces for the manufacture of alloy steels from virgin materials. In these furnaces, heat is produced within the metal by means of induced eddy currents. An additional advantage in these furnaces is that the molten metal undergoes continuous stirring by means of the induced currents.

## 7. Heat Treatment of Steels

The mechanical properties of steels, *e.g.*, hardness, elasticity, tensile strength, etc., can be varied as desired by proper heat-treatment, that is, by heating and cooling the steel under definite conditions. The important types of heat-treatment are—

**1. Annealing**. This involves *heating steel to a bright red heat and then allowing it to cool slowly*. As a result, the steel becomes soft and pliable. Annealed steel wears better than wrought iron.

2. **Hardening**. This involves *heating steel to a temperature below red heat and then cooling it rapidly by plunging in oil or water* (*quenching*). This makes steel very hard but brittle at the same time.

3. **Tempering**. This treatment consists in *reheating the hardened steel to a definite temperature* (*lower than before*) and then cooling it slowly. As a result, the hardened steel becomes softer and loses its brittleness. Any desired degree of hardness may be produced in the steel by reheating to a proper temperature.

4. **Case hardening**. This is the process of *heating soft, tough, low-carbon steel in contact with charcoal and then quenching in oil whereby the surface is hardened.* Case hardened steel is used for making shafts, gears, files, etc., which need a hard wearing surface, resistant to wear, but a tough interior resilient enough to withstand shock.

5. **Nitriding**. This is the modern process for the case-hardening of steels. It involves *heating alloy steels in an atmosphere of ammonia gas at500–600°C*. The nitrogen formed by the decomposition of ammonia combines with iron to form a very hard material, iron nitride. This substance makes the surface of the steel extremely hard and resistant to corrosion. The period of heating in ammonia varies from a few hours to a few days depending upon the depth to which the hardening is needed. The process of nitriding is superior to case hardening, as it requires a much lower temperature at which the steel object does not undergo distortion in shape.

## 8. Classification of Steels

Two important classes of steels are : (1) the carbon steels, and (2) the alloy steels.

**8-1. The Carbon steels**. Such steels have carbon as the only one alloying element; other elements may be present in traces but they do not affect the properties. According to the amount of carbon present, the carbon steels are of three types :

*a. Mild steels*. These are steels of low carbon content (from 0·05 to 0·25 per cent). These are quite ductile and similar to wrought iron in mechanical properties. These are used in the manufacture of bridge girders. automobiles, ships, buildings, rails, etc.

*b. Medium steels*. These steels contain 0·25 to 0·75 per cent carbon. These are harder than mild steel. Both mild and medium steels can be welded. Medium steels are used for making automobile axles, rails, car wheels—sometimes after proper heat-treatment.

*c. Hards steels*. Hard steels contain 0·75 to 1·5 per cent carbon. These are very hard and brittle, and cannot be welded. These are used, after proper heat-treatment, for making tools, springs, etc.

**8-2. Alloy steels**. These are steels to which certain metals or non metals have been added in quantities sufficient to produce special properties. Alloy steels are prepared by introducing the alloying elements into molten steel to improve it for special uses. Different alloy steels have different properties, and based upon them, different uses. *Stainless steel* is a well known alloy steel which contains 7-8% nickel, 14-18% chromium, and the rest iron. It is highly resistant to corrosion and is used for making cutlery, kitchenware, surgical instruments, etc. *Chrome-vanadium steel* (1-10% Cr, 0·15% V, rest iron) withstands strains and shocks without breaking. Two other metals used for the manufacture of alloy steels are manganese and molybdenum.

## 9. Pure Iron

Very pure iron is difficult to make. It may be obtained by means of the following reactions :

(1) By reducing pure iron (III) oxide in hydrogen at 1000°C.

$$Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O \uparrow$$

Pure iron (III) oxide is obtained by heating recrystallised ferric nitrate [$4Fe(NO_3)_2 \rightarrow 2Fe_2O_3 + 8NO_2 \uparrow + O_2 \uparrow$].

(2) By melting in vacuum the iron obtained by the electrolysis of a solution of iron (III) sulphate, iron (II) chloride, or iron (II) ammonium sulphate.

## 10. Physical Properties of Iron

(1) Pure iron is a silvery white lustrous metal resembling platinum in appearance. It is capable of taking a high polish.

(2) It is a heavy metal, density = 7·87. It has a high m.p., 1537°C.

(3) It is ductile, relatively soft, and possesses high tensile strength.

(4) Iron is highly magnetic but does not retain magnetism.

All these properties are greatly modified by the amount and nature of impurities, especially carbon, present in iron.

## 11. Reactions of Iron

(1) Iron is stable in dry air at atmospheric temperature. When heated in air, it gets covered with a thick, bluish-black scale of ferroso-ferric oxide or iron (II, III) oxide, $Fe_3O_4$, also called the magnetic oxide. When heated in oxygen in the form of powder or steel wool, iron burns brilliantly to form $Fe_3O_4$.

(2) Pure iron does not rust in air or in contact with water. Ordinary commercial iron rusts in moist air and under water containing dissolved oxygen forming partially hydrated iron (III) oxide, $Fe_2O_3.xH_2O$.

(3) When iron is heated in steam, it is oxidized to ferrosoferric oxide; hydrogen is set free.

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2 \uparrow$$

(4) Iron dissolves in hydrochloric acid and dilute sulphuric acid forming iron (II) ions, $Fe^{2+}$, and hydrogen.

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$$

Hot concentrated sulphuric acid forms $Fe^{3+}$, and $SO_2$ is evolved.

$$2Fe + 6H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 6H_2O + 3SO_2\uparrow$$

or, $$2Fe + 12H^+ + 3SO_4^{2-} \rightarrow 2Fe^{3+} + 6H_2O + 3SO_2\uparrow$$

Cold concentrated nitric acid has little effect on iron. Probably, a tough film of magnetic oxide is formed on the surface, which prevents further action. In fact, iron, after treatment with cold concentrated nitric acid, will not react with dilute acids in which it would otherwise readily dissolve. Such inactive iron is said to be passive. If passive iron is struck, or scratched, the oxide film is apparently broken, and the iron regains its activity. The same result is obtained by treating passive iron with reducing agents.

(5) Iron combines directly with sulphur, chlorine, bromine, and carbon to form respectively ferrous sulphide, FeS, ferric chloride, $FeCl_3$, ferroso-ferric bromide, $Fe_3Br_8$, and iron carbide, $Fe_3C$.

## 12. The Rusting of Iron

All forms of iron corrode, or rust, in moist air. That is, they get covered with a reddish-brown deposit of hydrated iron (III) oxide, $Fe_2O_3.xH_2O$, called rust. The rust that forms is loose and scales off, leaving the metal underneath exposed to corrosion by moist air. It therefore, offers no protection, and the process continues until all the metal is convered to rust. The following facts regarding rusting of iron are noteworthy :

(1) Iron does not rust in dry air, nor in water which is free from dissolved oxygen. This shows that both air and water are involved in the rusting process.

(2) Rusting proceeds very showly in pure water, the presence of dissolved electrolytes accelerates rusting. In moist air, the electroyte is simply carbonic acid, $H_2CO_3$, formed when carbon dioxide dissolves in air. Of course a strong electrolyte such as NaCl would be more effective (iron rusts faster in salt water than in fresh water). Rusting is very rapid in acid solutions; while the presence of alkalis slackens it.

(3) Iron in contact with a less active metal such as tin, lead, or copper rusts more rapidly than when alone, or when in contact with a more active metal such as zinc.

(4) Absolutely pure iron does not rust, an impurity in the iron is essential for rusting.

All these facts point towards rusting being an electrochemical process. Since all ordinary forms of commercial iron lack a uniformity of surface, millions of tiny electrochemical cells come into action on the iron surface exposed to moist air. The more active iron acts as the cathode and its impurity, generally carbon or iron carbide particles, acts as the anode. The electrode reactions that take place are :

At the anode ; $Fe \rightarrow Fe^{2+} + 2e^-$

At the cathode : $2H_2O \rightarrow 2H^+ + 2OH^-$

$$2H^+ + 2e^- \rightarrow H_2$$

The accumulation of hydrogen on the surface of iron tends to polarize the cell and stop the cell action. However, dissolved oxygen removes hydrogen as soon as it is formed by oxidation to water ($4H + O_2 \rightarrow 2H_2O$), and the electrochemical action continues. The iron (II) ions, $Fe^{2+}$, combine with the $OH^-$ ions of the electrolytic solution to form $Fe(OH)_2$.

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$

The iron (II) hydroxide is readily oxidized by air to hydrated iron (III) hydroxide, ($Fe(OH)_3$.

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$$

Gradually, $Fe(OH)_3$ loses water to yield a partially hydrated oxide, $Fe_2O_3.xH_2O$, which is iron rust.

**12-1 Prevention of rusting.** Iron can be protected against rusting by the following methods :

1. *By coating it with a suitable material.* This may be—

(*i*) an organic material such as paint, lacquer, grease, etc.,

(*ii*) another metal, *e.g.*, zinc, chromium, nickel, tin, cadmium, etc.,

(*iii*) a ceramic enamel, like that used on sinks, bathtubs, etc.,

(*iv*) a film of phosphate, produced by dipping iron into a hot alkaline solution of sodium phosphate; the phosphate forms a thin coating of basic phosphate of iron.

2. *By treating the red-hot surface with superheated steam* when a thin layer of magnetic iron oxide, $Fe_3O_4$, is formed ($3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$). This layer is adherent and non-porous, andprotects the metal underneath from rusting. The product, called Russia iron, is used for making stove pipes.

3. *By attaching a more active metal.* Underground iron pipes are protected from rusting by attaching blocks of a more active metal, *e.g.*, aluminium or magnesium. The more active metal becomes the negative pole and corrodes ($Mg \rightarrow Mg^{2+} + 2e^-$) rather than the iron. At the iron pole, reduction occurs, and so no $Fe^{2+}$ ions are produced. Magnesium rods are sometimes placed in hot water heaters where electrochemical action between iron and copper or brass fitting would cause the iron to rust.

4. *By alloying with suitable elements*. Alloys of iron with certain other elements are often corrosion resistant. Typical examples are duriron (Fe and Si) and stainless steel (Fe, Cr, and Ni).

## 13. Compounds of Iron

Iron forms two series of compounds : (1) Iron (II) or ferrous compounds in which iron is divalent, and (2) Iron (III) or ferric compounds in which iron is trivalent. Iron (II) salts gradually pass into iron (III) salts on exposure to air. The chief characteristics of the two series of compounds are summarized in table.

**Table 9-5** *Chief characteristics of iron (II) and iron (III) compounds*

| *Property* | *Iron (II) compounds* | *Iron (III) compounds* |
|---|---|---|
| (1) Colour | Anhydrous—white; hydrated—light green; in solution—nearly colourless. | White, yellow, or reddish-brown. |
| (2) Hydroxide | Light green; weak base. | Reddish brown; much weaker base. |
| (3) Reducing/oxidizing agent | Reducing agents; easily oxidized to ferric state. | Oxidizing agents; easily reduced to ferrous state. |

## 14. Oxides and Hydroxides of Iron

**14-1 Iron (II) oxide, ferrous oxide, FeO**. This may be obtained as a black powder by heating iron (II) oxalate in the absence of air.

$$\underset{\text{iron (II) oxalate}}{(COO)_2Fe.3H_2O} \xrightarrow{\Delta} \underset{\text{iron (II) oxide}}{FeO} + CO\uparrow + CO_2\uparrow + 3H_2O\uparrow$$

It is of little importance since it changes rapidly, when it is exposed to the air, into iron (III) oxide, $Fe_2O_3$. Iron (II) oxide is a basic oxide readily reacting with dilute acids to form the corresponding iron (II) salts.

$$FeO + 2H^+ \rightarrow Fe^{2+} + H_2O$$

*e.g.*, $$FeO + H_2SO_4 \rightarrow FeSO_4 + H_2O$$

**14-2. Iron (II) hydroxide, ferrous hydroxide, $Fe(OH)_2$.** It is obtained as a white precipitate upon the addition of alkali hydroxides to the solutions of iron (II) salts.

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2\downarrow$$

In the air the white hydroxide quickly turns green and then reddish-brown, by oxidation to iron (III) hydroxide.

$$4Fe(OH)_2 + \underset{\text{from air}}{O_2} + 2H_2O \rightarrow 4Fe(OH)_3$$

Iron (II) hydroxide, unlike iron (III) hydroxide, is soluble in the solutions of ammonium salts, *e.g.*, ammonium chloride. It is, therefore, necessary in the Group separation of metals in qualitative analysis to oxidize any iron present to the iron (III) state before adding ammonium chloride and ammonium hydroxide for the precipitation of Group (III) hydroxides. This oxidation is affected by boiling the filtrate from Group II with a few drops of concentrated nitric acid.

**14-3. Iron (III) oxide, ferric oxide, $Fe_2O_3$.** This oxide occurs in nature as the mineral hematite. It may be prepared in the laboratory by igniting iron (III) hydroxide,

$$2Fe(OH)_3 \xrightarrow{\Delta} Fe_2O_3 + 3H_2O \uparrow$$

or by heating iron (II) sulphate strongly.

$$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 \uparrow + SO_3 \uparrow$$

Iron (III) oxide is a red powder which reacts with acids to form the corresponding iron (III) salts.

$$Fe_2O_3 + 6H^+ \rightarrow 2Fe^{3+} + 3H_2O$$

It is used as a cheap red paint pigment under the names "Venetian red" and "red ochre". It is also used as an abrasive for grinding and polishing glass under the name of *rouge*.

**14-4. Iron (III) hydroxide, ferric hydroxide $Fe(OH)_3$.** It is formed as a reddish-brown gelatinous precipitate when a solution of alkali hydroxide or ammonium hydroxide is added to the solution of an iron (III) salt.

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \downarrow$$

On allowing the precipate to dry, iron (III) hydroxide is dehydrated to iron (III) oxide.

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$$

Iron (III) oxide is a weak base which is insoluble in alkali solutions. It dissolves in acids forming the corresponding iron (III) salts, including a carbonate, bicarbonate, and a sulphide.

$$Fe(OH)_3 + 3H^+ \rightarrow Fe^{3+} + 3H_2O$$

**14-5. Iron (II, III) oxide, ferroso-ferric oxide, $Fe_3O_4$.** This oxide occurs in nature as a magnetite or lodestone. It is made by heating iron to redness in air or steam.

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \uparrow$$

Iron (II, III) oxide is highly magnetic and is, therefore, called magnetic oxide of iron. When treated with acids, it yields the corresponding iron (II) and iron (III) salts in solution. This shows that it is a mixed oxide, $FeO.Fe_2O_3$.

## 15. Iron (II) salts

**15-1. Iron (II) chloride, ferrous chloride, $FeCl_2$.** The hydrated salt, $FeCl_2.4H_2O$, is obtained as blue-green crystals by dissolving iron in hydrochloric acid in the absence of air and concentrating the solution to the point of crystallization. The anhydrous salt is made by passing dry hydrogen chloride over red-hot iron fillings.

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$

Anhydrous iron (II) chloride is a deliquescent, white solid, which is very soluble in water.

**15-2. Iron (II) carbonate, ferrous carbonate, $FeCO_3$.** This occurs in nature in the mineral siderite or spathic iron ore. It may be produced as a white precipitate by the interaction of alkali carbonates (*e.g*, $Na_2CO_3$) and solutions of iron (II) salts in the absence of air.

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3 \downarrow$$

Iron (II) carbonate is insoluble in water but dissolves in water containing carbon dioxide forming the hydrogen carbonate.

$$FeCO_3 + H_2O + CO_2 \rightleftharpoons Fe(HCO_3)_2$$

On exposure to the air this solution loses carbon dioxide reforming iron (II) carbonate. The latter, however, is hydrolyzed and oxidized, depositing red-brown hydrated iron (III) oxide. Probably similar changes occurs when iron rusts.

**15-3. Iron (II) sulphide, ferrous sulphide, FeS.** It is precipitated when an alkali sulphide (*e.g.*, $Na_2S$) is added to a solution of an iron (II) salt.

$$Fe^{2+} + S^{2-} \rightarrow FeS \downarrow$$

It is made commercially by melting together iron and sulphur. The commercial samples are grey-black in colour and usually contain appreciable amounts of uncombined iron.

Iron (II) sulphide reacts with dilute acids forming an iron (II) salt in solution and hydrogen sulphide gas.

$$FeS + 2H^+ \rightarrow Fe^{2+} + H_2S \uparrow$$

*e.g.*, $$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S \uparrow$$

**15-4. Iron (II) sulphate, ferrous sulphate, $FeSO_4$.** It is the most important and well-known iron (II) salt.

*Preparation.* It is prepared in the laboratory by dissolving iron in dilute sulphuric acid. The solution is concentrated and cooled when pale-green crystals of iron (II) sulphate heptahydrate are deposited.

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2 \uparrow$$

However, the product is usually contaminated with iron (III) sulphate formed by oxidation and, hence, air-free acid should be used in this preparation. This compound is made commercially by evaporating the residual liquids from the pickling baths (originally containing sulphuric acid) used for dissolving out the oxide layer on mild sheets prior to galvanizing and tinplating. It is called in commerce "green vitriol" (हरा कसीस).

*Properties and reactions.* (1) Iron (II) sulphate is a light green, crystalline, efflorescent substance (*i.e.*, it loses water of hydration when exposed to air).

(2) On exposure to the air it slowly turns yellow by partial oxidation to basic iron (III) sulphate.

$$4FeSO_4 + 2H_2O + O_2 \rightarrow \underset{\text{basic iron (III) sulphate}}{4Fe(OH)SO_4}$$

(3) On heating, iron (II) sulphate first loses water of crystallization at 300°C, and at higher temperatures decomposes into iron (III) oxide, sulphur dioxide, and sulphur trioxide.

$$FeSO_4.7H_2O \xrightarrow{300°C} FeSO_4 + 7H_2O\uparrow$$

$$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2\uparrow + SO_3\uparrow$$

(4) Aqueous solutions of iron (II) sulphate readily absorb nitric oxide and turn black due to the formation of nitroso iron (II) sulphate $FeSO_4.NO$. This substance decomposes on heating with the liberation of nitric oxide (*ring test for nitrates*).

(5) Iron (II) sulphate forms a double salt with ammonium sulphate known as ferrous ammonium sulphate or Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$. This double salt is less soluble in water than ferrous sulphate and therefore can be obtained in a higher degree of purity. Moreover, in solution Mohr's salt is less readily oxidized by air. It is, therefore, used in volumetric analysis in preference to iron (II) sulphate.

(6) It also forms double salts with the sulphates of alkali metals. These double salts may be represented by the general formula, $FeSO_4.R_2SO_4.6H_2O$, where R stands for the alkali metal.

(7) Iron (II) sulphate is a powerful reducing agent and is itself oxidized to the iron (III) sulphate in redox reactions. Thus, it decolourises acidified solutions of potassium permanganate in cold.

$$5\times[Fe^{2+} \rightarrow Fe^{3+} + e^- \textit{ (oxidation of } FeSO_4\textit{)}$$

$$\underline{MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \textit{ (reduction of } KMnO_4\textit{)}}$$

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3} + Mn^{2+} + 4H_2O$$

or, $10FeSO_4 + 2KMnO_4 + 8H_2SO_4$
$\rightarrow 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$

*Uses.* Iron (II) sulphate is used (*i*) as a deodorant, (*ii*) as a disinfectant, (*iii*) as a weed-killer, (*iv*) as a wood preservative, (*v*) in the manufactures of inks, dyes, and pigments, (*vi*) as a mordant in dyeing and tanning industries, (*vii*) as a substitute of aluminium sulphate in the purification of water.

## 16. Iron (III) Salts

**16-1. Iron (III) sulphate, ferric sulphate, $Fe_2(SO_4)_3$.** It is made by heating iron (II) sulphate with concentrated sulphuric acid.

$$2FeSO_4 + 2H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2H_2O + SO_2\uparrow$$

Iron (III) sulphate is a pale brown powder. It dissolves in water but the solutions are acidic owing to hydrolysis. It forms double sulphates or alums with the sulphates of monovalent metals or with ammonium sulphate. Of these, potash iron alum, $K_2SO_4.Fe_2(SO_4)_3.24H_2O$, and ammonium iron alum, $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$, are the best known, and both of these are exclusively used as mordants in dyeing.

When heated strongly, iron (III) sulphate decomposes to give iron (III) oxide and sulphur trioxide.

$$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3\uparrow$$

**16-2. Iron (III) chloride, ferric chloride, $FeCl_3$.** This is the most important and well known of all iron (III) compounds.

*Preparation.* (1) The hydrated salt can be made by dissolving iron in hydrochloric acid in the presence of chlorine. On concentrating and cooling, the solution deposits yellow crystals of iron (III) chloride hexahydrate, $FeCl_3.6H_2O$.

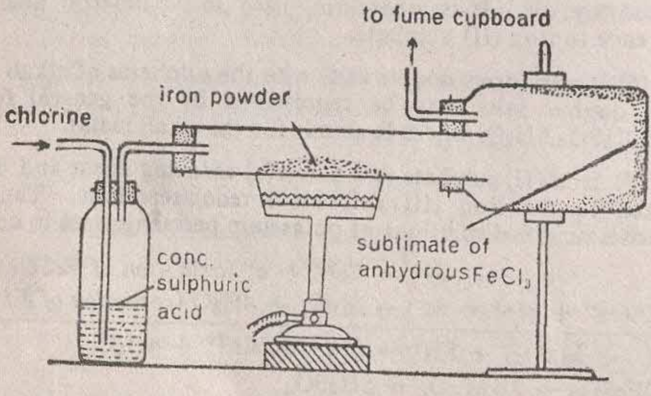


Fig. 14-7. Preparation of anhydrous iron (III) chloride.

(2) The anhydrous compound is made by passing dry chlorine over heated iron, and condensing the iron (III) chloride, which sublimes at 315°C, in a cooled receiver (Fig. 14·7).

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3$$

*Properties and reactions.* (1) Iron (III) chloride is not a salt (*i.e.*, an ionic compound) but is covalent, as indicated by its volatility and solubility in non-polar solvents such as ether and alcohol. However, it dissolves in water to give $Fe^{3+}$ and $Cl^-$ ions.

(2) It is highly deliquescent and very soluble in water, forming a brown solution which gives an acid reaction by hydrolysis, and produces a colloidal solution of iron (III) hydroxide on standing.

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$$

(3) The vapour density of the anhydrous salt at 450°C corresponds to the formula $Fe_2Cl_6$. At higher temperatures the $Fe_2Cl_6$ dissociate into $FeCl_3$ molecules so that the vapour density progressively decreases on heating and corresponds to the formula $FeCl_3$ at 750°C. At higher temperatures the vapour density further decreases, probably due to the dissociation of iron (III) chloride into iron (II) chloride and chlorine.

$$Fe_2Cl_6 \overset{750^\circ}{\rightleftharpoons} 2FeCl_3 \overset{\text{above } 750^\circ}{\rightleftharpoons} 2FeCl_2 + Cl_2\uparrow$$

(4) Iron (III) chloride forms a number of double salts, *e.g.*, $2KCl.FeCl_3.H_2O$, etc.

(5) When heated in a current of hydrogen, iron (III) chloride is reduced to ferrous chloride.

$$2FeCl_3 + H_2 \rightarrow 2FeCl_2 + 2HCl$$

(6) Iron (III) chloride readily liberates iodine from potassium iodide solution, behaving as an oxidizing agent.

$$2FeCl_3 + 2KI \rightleftharpoons 2FeCl_2 + 2KCl + I_2$$

(7) On heating hydrated iron (III) chloride, iron (III) oxide is formed, water and hydrogen chloride being liberated in the change.

$$2[FeCl_3.6H_2O] \xrightarrow{\Delta} Fe_2O_3 + 9H_2O + 6HCl$$

Anhydrous iron (III) chloride, therefore, cannot be obtained by heating the hydrated compound.

*Uses.* Hydrated iron (III) chloride is used in medicine (*i*) to coagulate blood and thus stop bleeding, and (*ii*) in the treatment of anaemia. It is also used as a mordant, and in the manufacture of pigments and dyes.

## 17. Distinction Between Iron (II) and Iron (III) Compounds

Compounds of iron may be distinguished as iron (II) or iron (III) compounds by the tests given in table 14-2.

**Table 14-2.** *Tests for iron (II) and iron (III) compounds*

| *Reagent* | *Iron (II) salt solution* | *Iron (III) salt solution* |
|---|---|---|
| 1. Sodium hydroxide solution | White ppt., turning green and then brown | Reddish-brown, gelatinous ppt |
| 2. Potassium ferrocyanide solution. | White or pale-blue ppt. | Deep blue ppt. |
| 3. Potassium ferrocyanide solution | Deep blue ppt. | Brown solution |
| 4. Potassium thiocyanate solution | No pronounced colour change | Blood-red colour |
| 5. Hydrogen sulphide | Black ppt. of FeS | Pale yellow ppt. of sulphur |

## II. COPPER

## 18. Copper in Nature

Copper does occur native but only infrequently. Its common ores are :

(*i*) *Sulphides* such as *copper glance*, $Cu_2S$, and *copper pyrites or chalcopyrite*, $CuFeS_2$ (or, $CuS.FeS$).

(*ii*) *Oxides*, such as *cuprite*, $Cu_2O$ and *melaconite*, $CuO$.

(*iii*) *Carbonates*, such as *malachite*, $CuCO_3.Cu(OH)_2$, and *azurite* $2CuCO_3.Cu(OH)_2$.

The ore copper pyrites is the chief source of copper.

## 19. Extraction of Copper

**19-1. From the oxide and carbonate ores.** The *low grade ores* are leached with dilute sulphuric acid. Copper is extracted from the resulting copper sulphate solution either by electrolysis or by treatment with scrap iron.

$$\underset{\text{(cuprite)}}{CuO} + H_2SO_4 \rightarrow CuSO_4 + H_2O$$

$$\underset{\text{(malachite)}}{CuCO_3.Cu(OH)_2} + 2H_2SO_4 \rightarrow 2CuSO_4 + 3H_2O + CO_2$$

$$CuSO_4 + Fe \rightarrow Cu\downarrow + FeSO_4$$

*High grade ores* are heated with coke and a suitable flux. Copper oxide present as such or produced by the decomposition of the carbonate is reduced to metallic copper.

$$CuCO_3 \rightarrow CuO + CO_2\uparrow$$

$$CuO + C \rightarrow Cu + CO\uparrow$$

**19-2. From sulphide ores.** The various steps are :

(1) *Concentration.* The ore is mechanically ground to a fine powder and concentrated by flotation.

(2) *Roasting*. The concentrates are roasted in air at a red heat. As a result of this, (*i*) the impurities of arsenic and antimony volatilize as the oxides $As_2O_3$ and $Sb_2O_3$ respectively, (*ii*) copper pyrites are converted into copper (I) sulphide and iron (II) sulphide, and (*iii*) part of the iron (I) sulphide is converted into iron (I) oxide.

$$\underset{\text{copper pyrites}}{2CuFeS_2} + \underset{\text{from air}}{O_2} \longrightarrow \underset{\text{copper (I) sulphide}}{Cu_2S} + \underset{\text{iron (II) sulphide}}{2FeS} + SO_2\uparrow$$

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2\uparrow$$

Thus, the roasted mass is a mixture of chiefly $Cu_2S$, FeS, and FeO.

(*3*) *Smelting* (*production of matte*). The roasted ore is mixed with sand and smelted in a *reverberatory furnace*. Most of the remaining iron sulphide is converted into the oxide which reacts with the silica, forming a fusible slag of iron silicate, $FeSiO_3$.

$$FeO + SiO_2 \rightarrow FeSiO_3 \text{ (Fusible slag)}$$

The slag floats over a molten layer consisting chiefly of copper (I) sulphide with a little iron sulphide, called *matte*. The upper layer of molten slag is continuously run off.

(*4*) *Bessemerisation* (*conversion of matte to blister copper*). The molten matte is introduced into a Bessemer converted (Fig. 14-4) lined with lime or magnesium oxide. A pre-calculated amount of sand is added and a blast of air blown through the mixture. The iron (II) sulphide undergoes oxidation to produce iron (II) oxide which is removed as the ferrous silicate, $FeSiO_3$, slag.

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2\uparrow$$

$$FeO + SiO_3 \rightarrow FeSiO_3$$

After all iron is removed, the air blast begins to change copper (I) sulphide into copper (I) oxide which immediately reacts with unchanged copper (I) sulphide to give molten copper.

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2\uparrow$$

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2\uparrow$$

The metallic copper then melts and sinks to the bottom of the converter. It is poured out into steel moulds. As it cools, the sulphur dioxide dissolved in it escapes, giving a blistered appearance to the solidified metal. Hence the product is called *blister copper*. It contains 97-98 per cent copper.

(*5*) *Refining of blister copper*. Blister copper contains 2-3 per cent of various impurities, such as iron, nickel, zinc, lead, silver, gold, etc. It is refined by the following two processes :

*a*. *Furnance refining* (*poling*). Blister copper is remelted in a reverberatory furnace in a stream of air. The impurities of sulphur, arsenic, antimony, lead, and zinc volatilize as their oxides. Baser metals such as iron, nickel, etc. from a scum of oxides which is skimmed off the surface. The molten copper is then stirred with poles of green wood which chars giving off reducing gases. These gases reduce to copper any copper oxide formed. The product is 99·5 per cent pure and suitable for the preparation of copper alloys.

Very pure copper needed for electrical use is obtained by the electrolytic method.

*b. Electrolytic refining.* Slabs of impure copper are suspended as anodes between the cathodes of thin pure copper sheets in a cell containing 15 per cent copper sulphate solution acidified with sulphuric acid. When a direct current passes through the electrolyte, the $Cu^{2+}$ ions in solution migrate to the cathode and are discharged their as copper atoms ($Cu^{2+} + 2e^- \rightarrow Cu$). The copper atoms from the anode lose two electrons and enter the solution as $Cu^{2+}$ ions ($Cu - 2e^- \rightarrow Cu^{2+}$). Thus, in effect, copper atoms are 'peeled off' the anode and deposited on the cathode. Impurities which are more active than copper (Zn, Fe, Ni, etc.) are also converted to their ions. However, these ions remain in solution while the ions of copper, low in the activity series, are more easily reduced at the cathode. The impurities of less active metals, such as silver and gold remains as their atoms and drop to the bottom as the copper atoms change to their ions at the anode. The fine particles of these metals collect as *anode mud* at the base of the anode. The anode mud is washed out of the electrolytic tank, dried, and worked for the recovery of its gold and silver content.

The electrolytically refined copper is about 99·95 per cent pure. The value of the precious metals recovered from the anode mud nearly pays the cost of electrolytic refining.

In India, Copper is being manufactured by Hindustan Copper Ltd. in Bihar, Madhya Pradesh and Rajasthan.

## 20. Phyical Properties of Copper

1. Copper is a heavy (sp. gr. 8·94), lustrous metal with a reddish-brown tinge. It melts at 1083°C and boils at 2820°C.

2. It is highly melleable and ductile, and can be easily fashioned into sheets, wires, and tubings

3. It is an excellent conductor of heat and electricity, second only to silver in this respect. Its electrical conductivity is greatly reduced by the presence of even traces of metal impurities. Hence, copper for electrical purpose, must be extremely pure.

4. Copper readily alloys with many metals.

## 21. Reactions of Copper

**1. Action of air.** On standing in *dry air* at room temperature copper is very slowly tarnished due to the formation of an extremely thin film of oxide on the surface which prevents it from further oxidation. When heated strongly in air copper is converted into black copper (II) oxide, CuO. In *moist air*, a greenish deposit of basic copper carbonate, $CuCO_2.Cu(OH)_2$, is formed on its surface by the combined action of moisture, oxygen, and carbon dioxide.

$$2Cu + H_2O + O_2 + CO_2 \rightarrow Cu(OH)_2\,CuCO_3$$

**2. Action of water.** Copper does not react with water at any temperature. It dissociates steam at while heat to a very small extent.

**3. Combination with non-metals.** Copper readily combines with chlorine and sulphur at higher temperatures forming $CuCl_2$ and CuS respectively.

**4. With acids.** Being low in the electrochemical series, copper is not capable of displacing hydrogen from acids. It is unaffected by dilute hydrochloric and sulphuric acids in the absence of air, but it dissolves readily in nitric acid of all concentrations.

*Dilute acid* : $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$

*Conc. acid* : $Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$

In the presence of air copper slowly dissolves in dilute hydrochloric acid and dilute sulphuric acid forming the corresponding salt and water.

$$2Cu + 4HCl + O_2 \rightarrow 2CuCl_2 + 2H_2O$$

$$2Cu + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O$$

With hot concentrated sulphuric acid, copper gives copper sulphate and sulphur dioxide.

$$Cu + 2H_2SO_4 \xrightarrow{\Delta} CuSO_4 + 2H_2O + SO_2$$

**5. Reducing action.** In the above reactions, copper reduces nitric acid to NO or $NO_2$ and sulphuric acid to $SO_2$. Copper also reduces iron (III) salts to iron (II) salts.

$$2Fe^{3+} + Cu \rightarrow 2Fe^{2+} + Cu^{2+}$$

$$e.g.,\ 2FeCl_3 + Cu \rightarrow 2FeCl_2 + CuCl_2$$

**6. Displacement of metals.** Copper displaces less electropositive metals such as silver, mercury, etc., from the solutions of their salts. For example,

$$Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag\downarrow$$

$$Cu + HgCl_2 \rightarrow CuCl_2 + Hg\downarrow$$

**7. Formation of complexes.** In the presence of air copper dissolves in aqueous solutions of ammonia and sodium (or potassium) cynide forming soluble complexes.

$$Cu + 4NH_3 + H_2O + [O] \rightarrow \underset{\text{tetrammine copper (II) hydroxide}}{[Cu(NH_3)_4](OH)_2}$$

$$Cu + 4KCN + H_2O + [O] \rightarrow \underset{\text{potassiun tetracyano-cuprate (II)}}{K_2[Cu(CN)_4]} + 2KOH$$

## 22. Uses of Copper

Owing to its attractive appearance, excellent workability, high thermal and electrical conductivity, resistance to corrosion, and its readiness to form alloys with other metals, copper is a metal of multifarious uses. Its important uses are :

(*i*) For making electrical wiring and other electric equipment.

(*ii*) For the manufacture of steam pipes, chemical plants, vacuum pans, calorimeters, condenser tubes, automobile radiators, boilers, and condensers in locomotives and ships.

(*iii*) As a roofing material for covering bottoms of wooden ships, and for roofing gutters, conductor pipes, etc.

(*iv*) In copper plating and electrotyping.

(*v*) For manufacturing alloys such as the bronze, brass, German silver, gun metal, bell metal, etc. 14-Carat gold has 30 per cent copper, added for hardening.

(*vi*) For the manufacture of copper compounds.

## 23. Compounds of Copper

Copper forms two series of compounds : copper (I) or *cuprous* in which it is monovalent and copper (II) or *cupric* in which it is divalent. Both cuprous any cupric compounds are more commonly formed covalently rather than electrovalently. At high temperatures copper (II) salts are less stable than copper (I) salts and change into the corresponding copper (I) salts. Copper (II) salts containing weakly electronegative anions, *e.g.*, $I^-$, $CN^-$, $CNS^-$, etc., decompose instantaneously into the corresponding copper (I) compounds. This is because such anions readily transfer one electron to the copper (II) ion which has only 17 electron in its now outermost shell and hence, ready to accept an electron. When the electron transfer has taken place, the free radicals or atoms from the anions unite in pairs to form covalent molecules. For example,

$$Cu^{2+} + I^- \rightarrow Cu^+ + I \; ; I + I \rightarrow I_2$$

Copper (I) and copper (II) ions are related each other in solution as $2Cu^+ \rightleftharpoons Cu^{2+} + Cu$.

Copper (II) salts are often named as simply copper salts.

## 24. Copper (I) Oxide, Cuprous Oxide, $Cu_2O$

*Preparation.* It is best prepared by boiling alkaine copper sulphate solution or better still, Fehling's solution ($CuSO_4$ + NaOH + sodium hydrogen tartarate) with a reducing agent *e.g.*, glucose.

$$2CuSO_4 + 4NaOH + 2[H] \rightarrow Cu_2O\downarrow + 2Na_2SO_4 + 3H_2O$$

*Properties.* It is a yellow or red powder depending on the particle size. It is insoluble in water but dissolves readily in ammonia solution in the absence of air giving a colourless solution containing *diammine copper (I) hydroxide*, $[Cu(NH_3)_2]OH$. It also dissolves in acids forming copper (I) salts which are stable only if they form a complex with the acid as in the case of hydrochloric acid.

$$Cu_2O + 2HCl \rightarrow 2CuCl\downarrow + H_2O$$

$$CuCl + HCl \rightarrow \underset{\text{cuprochlorous acid}}{H[CuCl_2]}$$

The copper (I) salts formed with sulphuric acid and nitric acid are unstable in solution and immediately decompose into the corresponding copper (II) salt and copper.

$$Cu_2O + H_2SO_4 \rightarrow CuSO_4 + Cu + H_2O$$

$$Cu_2O + 2HNO_3 \rightarrow Cu(NO_3)_2 + Cu + H_2O$$

*Uses.* (1) For making red glass. (2) In the manufacture of metal rectifiers.

## 25. Copper (II) Oxide, Cupric Oxide, CuO

*Preparation.* It is made by heating copper (II) hydroxide, carbonate or nitrate, or by heating the metal to about 800°C in air or oxygen.

$$Cu(OH)_2 \rightarrow CuO + H_2O\uparrow$$

$$CuCO_3 \rightarrow CuO + CO_2\uparrow$$

$$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2\uparrow + O_2\uparrow$$

$$2Cu + O_2 \rightarrow 2CuO$$

*Properties.* It is a hygroscopic black powder, insoluble in water. It decomposes above 1000°C into copper (I) oxide and oxygen.

$$4CuO \rightleftharpoons 2Cu_2O + O_2$$

It is a mild oxidizing agent and when heated with organic substances, it oxidizes their carbon to carbon dioxide and hydrogen to water.

$$CuO + H_2 \rightarrow Cu + H_2O$$

$$2CuO + C \rightarrow Cu + CO_2$$

Being a basic oxide it dissolves readily in acids forming copper (II) salts. For example,

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$$

Copper (II) oxide dissolves in ammonia solution forming tetrammine copper (II) hydroxide, $[Cu(NH_3)_4](OH)_2$.

*Uses.* (1) In organic analysis for the detection and estimation of hydrogen and carbon. (2) In petroleum refining. (3) In making blue glass and ceramics (it produces blue colour due to the formation of copper (II) silicate).

## 26. Copper (II) Hydroxide, Cupric Hydroxide, $Cu(OH)_2$

This is formed as a gelatinous pale-blue precipitate when sodium hydroxide solution is added to a copper (II) salt solution. For example,

$$CuSO_4 + 2NaOH \rightarrow Cu(OH)_2 \downarrow + Na_2SO_4$$

When suspended in water and boiled it changes to black hydrated copper (II) oxide. It dissolves in acids forming corresponding copper (II) salts and in ammonia solution forming $[Cu(NH_3)_4](OH)_2$.

*Uses.* The solution of copper (II) hydroxide in ammonia dissolves cellulose and is used in making artificial silk. The solution of cellulose is squirted through fine jets into an acid bath when the cellulose is precipitated as fine, long threads. These threads are washed, dried, and woven into cloth.

## 27. Copper (I) Chloride, Cuprous Chloride, CuCl

*Preparation.* (1) By heating copper (II) oxide, copper (II) chloride, or copper (II) sulphate with excess of copper turnings and concentrated hydrochloric acid.

$$CuO + Cu + 2HCl \rightarrow 2CuCl + H_2O$$

$$CuCl_2 + Cu \rightarrow 2CuCl$$

$$CuSO_4 + Cu + 2HCl \rightarrow 2CuCl + H_2SO_4$$

Copper (II) chloride dissolves in excess of hydrochloric acid forming a soluble complex $H[CuCl_2]$ but separates as a white precipitate on puring the solution into a large excess of cold water.

(2) By passing sulphur dioxide through a mixture of copper (II) sulphate and sodium chloride solutions.

$$2CuSO_4 + 2NaCl + SO_2 + 2H_2O \rightarrow 2CuCl \downarrow + 2NaHSO_4 + H_2SO_4$$

*Properties.* (1) It is a white crystalline solid, almost insoluble in water.

(2) It dissolves readily in concentrated hydrochloric acid forming $H[CuCl_2]$, and in ammonia solution forming $[Cu(NH_3)_2]Cl$. These solutions absorb carbon monoxide which forms colourless crystals of the carbonyl compound, $CuCl.CO.2H_2O$.

(3) In moist air, it is slowly oxidized to green basic copper (II) chloride, $3CuO.CuCl_2.3H_2O$.

(4) Oxidizing agents convert it into copper (II) chloride.

$$2CuCl + 2HCl + [O] \rightarrow 2CuCl_2 + H_2O$$

(5) An ammoniacal solution of copper (I) chloride reacts with acetylene to form a red precipitate of copper (I) acetylide, $Cu_2C_2$.

$$H.C{\equiv}C.H + Cu_2Cl_2 + 2NH_4OH \rightarrow Cu.C{\equiv}C.Cu \downarrow + 2NH_4Cl + 2H_2O$$

(6) It reacts with sodium hydroxide to give a yellow precipitate of copper (I) oxide which turns red on boiling.

$$Cu_2Cl_2 + 2NaOH \rightarrow Cu_2O\downarrow + 2NaCl + H_2O$$

(7) With $H_2S$, it gives black copper (I) sulphide.

$$Cu_2Cl_2 + H_2S \rightarrow Cu_2S\downarrow + 2HCl$$

*Structure*. Copper (I) chloride is largely a covalent compound. It is a very poor conductor in the fused state. Its vapour density at 1700°C corresponds to the double molecules $Cu_2Cl_2$. In the crystalline state it possesses non-ionic space lattices.

*Uses*. (1) In the gas analysis for absorbing carbon monoxide and acetylene.

(2) In the Sandmeyer reaction.

## 28. Copper (II) Chloride, Cupric Chloride, $CuCl_2$

*Preparation*. The anhydrous salt is made by the action of dry chlorine on heated copper. Hydrated salt, $CuCl_2.2H_2O$, is obtained by dissolving copper (II) oxide, $CuO$, or the basic copper carbonate, $Cu(OH)_2\,CuCO_3$, in concentrated hydrochloric acid, and concentrating the solution to the crystallization point.

*Properties*. The anhydrous salt is a brown powder ; the hydrated salt is in the form of green crystals which are deliquescent.

When heated to 800°C, the anhydrous salt dissociates into copper (I) chloride and chlorine.

$$2CuCl_2 \rightarrow 2CuCl + Cl_2$$

The solution of copper (II) chloride in concentrated hydrochloric acid is brownish-yellow owing to the preponderance of $[CuCl_4]^{2-}$ ions. On adding water, the solution becomes green because of the formation of the complex ion $[Cu(H_2O)_4]^{2+}$ which is blue. On further dilution, the solution turns pale blue owing to the preponderance of blue $[Cu(H_2O)_4]^{2+}$ ion. These colour changes are reversed on adding the concentrated hydrochloric acid.

$$\begin{array}{lll} \textit{In conc. HCl}: & Cu^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} & \textit{yellow} \\ \textit{In dilute HCl}: & \begin{array}{l} Cu^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} \\ Cu^{2+} + 4H_2O \rightleftharpoons [Cu(H_2O)_4]^{2+} \end{array} & \left.\begin{array}{r} \textit{yellow} \\ \textit{blue} \end{array}\right\} \textit{green} \\ \textit{In water}: & Cu^{2+} + 2H_2O \rightleftharpoons [Cu(H_2O)_4]^{2+} & \textit{blue} \end{array}$$

## 29. Copper (II) Sulphate, $CuSO_4$

*Preparation*. It may be prepared by the action of sulphuric acid on copper, its oxide, hydroxide, or carbonate. On a commercial scale, it is made by spraying hot dilute sulphuric acid on to copper turnings packed in a lead-lined tower up which a current of air is blown.

$$2Cu + 2H_2SO_4 + O_2\,(air) \rightarrow 2CuSO_4 + 2H_2O$$

The liquid flowing out of tower is recirculated until all the acid is used up. It is then concentrated by evaporation when copper sulphate crystallizes out as deep blue pentahydrate, $CuSO_4.5H_2O$, called *blue vitriol.*

It is also manufactured by the controlled roasting of copper pyrites, $CuFeS_2$, in air and leaching out the resulting copper sulphate with water. Ferric oxide is left behind.

$$4CuFeS_2 + 15O_2 \rightarrow 4CuSO_4 + 2Fe_2O_3 + 4SO_2\uparrow$$

*Properties.* (1) It is a blue crystalline substance readily soluble in water. Its aqueous solution behaves acidic towards litmus due to hydrolysis.

(2) *Action of heat.* On heating, it loses four molecules of water of crystallization at 100°C and then the fifth one at 230°C. The anhydrous salts decomposes at 750°C to give copper (II) oxide and sulphur trioxide.

$$CuSO_4.5H_2O \overset{100°C}{\rightleftarrows} CuSO_4.H_2O \overset{250°C}{\rightleftarrows} CuSO_4 \overset{750°C}{\rightleftarrows} CuO + SO_3$$

The anhydrous salt regains blue colour when moistened with water.

(3) It forms double salts with alkali sulphates. For example, $K_2SO_4.CuSO_4.6H_2O$ and $(NH_4)_2SO_4.CuSO_4.6H_2O$.

(4) *Action of alkalis.* Caustic alkalis precipitate bluish-white copper hydroxide form solutions of copper salts.

$$CuSO_4 + 2NaOH \rightarrow Na_2SO_4 + Cu(OH)_2\downarrow$$

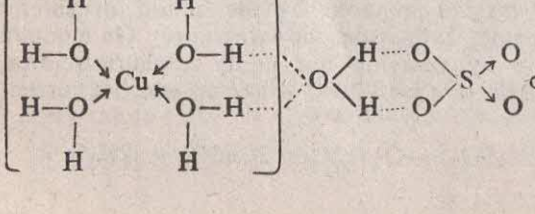
With ammonium hydroxide, the precipitate of copper hydroxide first formed dissolves in excess of ammonium hydroxide yielding a deep blue solution of tetrammine copper (II) sulphate, $[Cu(NH_3)_4].SO_4$. This solution, called Schweizer's reagent, is used for dissolving cellulose in the manufacture of artificial silk.

(5) It reacts with soluble iodides to give copper (I) iodide and iodine.

$$CuSO_4 + 2KI \rightarrow K_2SO_4 + CuI_2$$

$$\underset{\text{copper (II) iodide}}{2CuI_2} \rightarrow \underset{\text{copper (I) iodide}}{Cu_2I_2} + I_2$$

*Structure.* In copper sulphate pentahydrate, four of the water molecules are co-ordinated to the cupric ion; the fifth one is attached to the sulphate ion and to two of the co-ordinated water molecules by hydrogen bonds (dotted lines).



or $[Cu(H_2O)_4].SO_4.H_2O$

*Uses.* (1) In electroplating, electrotyping, and electrorefining of copper, and in electric batteries.

(2) As a mordant in dyeing and calico printing.

(3) For preserving timber.

(4) As a fungicide for fruit trees. For this purpose it is applied as solution mixed with milk of lime (Bordeaux mixture).

(5) In the preparation of other compounds of copper.

(6) Anhydrous copper sulphate is used for the detection of water and for the preparation of absolute alcohol.

## 30. Copper (II) Nitrate, $Cu(NO_3)_2$

It is prepared by dissolving copper, or its oxide or carbonate in nitric acid. On concentrating the solution, copper nitrate crystallizes out with three molecules of water of crystallization, as deep blue crystals.

On strong heating, it decomposes and leaves a residue of cupric oxide.

$$2Cu(NO_3)_2 \xrightarrow{\Delta} 2CuO + 4NO_2\uparrow + O_2\uparrow$$

## 31. Copper (II) Sulphide, CuS

It is obtained as a black precipitate when hydrogen sulphide is passed through the solution of a copper salt, *e.g.*, copper sulphate.

$$CuSO_4 + H_2S \rightarrow CuS\downarrow + H_2SO_4$$

It dissolves in hot, dilute acids forming the corresponding copper salts with the liberation of hydrogen sulphide.

### III. ZINC

## 32. Zinc in Nature

Zinc occurs only in the combined form. Its ores are widely distributed in nature. The important ores of zinc include the—

(*i*) *sulphide ore*, ZnS, called zinc blende,

(*ii*) *carbonate ore*, $ZnCO_3$, called calamine,

(*iii*) *oxide ore*, ZnO, called zincite, and

(*iv*) *silicate ore*, $2ZnO.SiO_2$ or $Zn_2SiO_4$, called willemite.

## 33. Extraction of Zinc

**1. Distillation process.** This process consists in converting the zinc compound in the ore to zinc oxide and reducing the latter to zinc by heating with carbon at 1300—1500°C

$$ZnO + C \rightarrow Zn + CO\uparrow$$

The sulphide ores are converted to zinc oxide by roasting at 800—1100°C in excess of air

$$\underset{\text{(in zinc blende)}}{2ZnS} + 3O_2 \rightarrow 2ZnO + 2SO_2\uparrow$$

The carbonate ore, calamine, gives oxide by simple calcination.

$$ZnCO_3 \rightarrow ZnO + CO_2\uparrow$$

**Reduction of zinc oxide.** Briquets made of zinc oxide (roasted ore), powdered coke (reducing agent and fuel), and clay (binder) are fed into a vertical retort made of sheet steel and lined with firebrick. The retort is heated externally to 1400-1500°C. The zinc vapour and carbon monoxide pass out through the exit near the top into the condensers where zinc condenses to give spelter. Carbon monoxide passes out and is used for heating the retorts. Fresh charge is continuously fed into the retort through the charging door (Fig. 14-8).

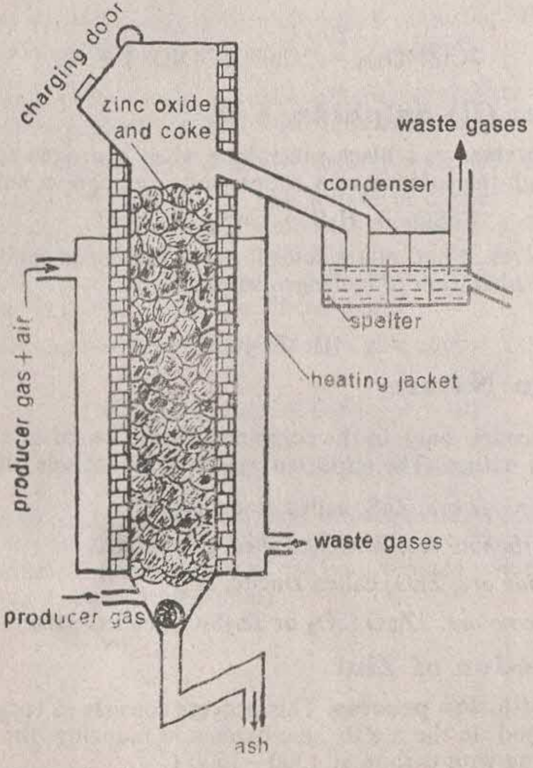


Fig. 14-8. The continuous vertical process for smelting of zinc.

The crude zinc obtained contains small amounts of cadmium, arsenic, iron and lead as impurities. It is purified by two methods :

(*i*) *By repeated distillations under reduced pressure.* The zinc vapour condenses to the metal of 99·99 per cent purity. Impurities are left behind.

(*ii*) *By electrolytic refining.* A slab of impure zinc is made the anode while pure zinc plate is made the cathode in an electrolytic bath of zinc sulphate solution acidified with sulphuric acid. On electrolysis, pure zinc from the electrolytic bath deposits on the cathode from which it is scrapped off at intervals. An equivalent amount of zinc from the anodes passes into the electrolyte.

2. **Electrolytic process**. This process consists in producing a solution of zinc sulphate from the ore which is then electrolysed to obtain zinc. The various steps are :

*i. Production of zinc sulphate solution.* The ore is roasted in special furnaces under such conditions that zinc sulphide is oxidized mainly to zinc sulphate, $ZnSO_4$. A little zinc oxide is also formed. The roasted ore is leached with sulphuric acid to dissolve the zinc sulphate and zinc oxide, which is also converted into zinc sulphate. The acid also dissolves the sulphates (except silver sulphate and lead sulphate) and the oxides of other metals present as impurities in the ore.

*ii. Precipitation of impurities.* The resulting solution is treated with powdered zinc which displaces copper, cadmium, arsenic, antimony, etc. Manganese and iron are precipitated as hydroxides by adding lime.

*iii. Electrolysis.* The purified solution of zinc sulphate is electrolysed using aluminium cathodes, lead anodes, and a high current density. Under these conditions only zinc ions are dicharged at the cathode where the pure metal is deposited. Sulphuric acid is regenerated as electrolysis proceeds and is used in the leaching of more roasted ore. The overall reaction is :

$$2ZnSO_4 + 2H_2O \rightarrow 2Zn + 2H_2SO_4 + O_2\uparrow$$

At intervals, the cathodes are removed and the deposited zinc (m.p. 419·5°C) separated from aluminium (m.p. 660°C) by melting. Molten zinc is cast into ingots.

Electrolytic process has the following advantages :

(1) It supplies zinc of 99·95 per cent purity.

(2) It can be applied to low grade ores.

(3) It permits recovery of any precious metals which are present as impurities.

## 34. Physical Properties of Zinc

Zinc is a bluish white, lustrous metal, m.p. 419·5°C, b.p. 907°C, soft enough to be marked with a knife. It is brittle at ordinary temperature but between 100-150°C it is both ductile and malleable. In this temperature range it may be drawn into wires or rolled into thin sheets and the metal does not become brittle on cooling. Zinc is a retalively poor conductor of heat and electricity, its conductivity being about one quarter that of silver in each case.

## 35. Reactions of Zinc

(1) *Action of air*. In moist air zinc becomes coated with a dull grey film of oxide and basic carbonate which protects the metal from further corrosion.

(2) *Burning*. When heated strongly in air or oxygen, zinc burns to oxide, ZnO.

$$2Zn + O_2 \rightarrow 2ZnO$$

(3) *Action of water*. It decomposes steam at red heat forming zinc oxide and hydrogen.

$$Zn + H_2O \rightarrow ZnO + H_2 \uparrow$$

(4) *Action of acids*. Pure zinc reacts hardly at all with dilute acids as a protective layer of hydrogen adheres on the surface. Impure zinc readily displaces hydrogen from dilute HCl or $H_2SO_4$.

$$Zn + H_2SO_4(dil.) \rightarrow ZnSO_4 + H_2 \uparrow$$

When heated with *conc.* $H_2SO_4$, zinc gives sulphur dioxide.

$$Zn + 2H_2SO_4 \rightarrow ZnSO_4 + 2H_2O + SO_2 \uparrow$$

The solution on concentration deposits crystals of $ZnSO_4.7H_2O$.

*With* $HNO_3$ it reacts forming zinc nitrate and a reduction product of nitric and depending on its concentration.

*i*. With very dil. $HNO_3$, ammonium nitrate is formed.

$$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

*ii*. With dil. $HNO_3$, nitrous oxide is evolved.

$$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O \uparrow$$

*iii*. With conc. $HNO_3$, nitrogen dioxide is formed.

$$Zn + 4HNO_3 \rightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2 \uparrow$$

(5) *Action of alkalis*. Zinc dissolves in boiling aqueous solutions of NaOH or KOH forming zincates and hydrogen.

$$Zn + 2NaOH \longrightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + H_2 \uparrow$$

(6) *Combination with non-metals.* Zinc combines exothermically with the halogens, sulphur, and phosphorous. At red heat it decomposes ammonia forming zinc nitride, $Zn_3N_2$.

$$Zn + Cl_2 \rightarrow ZnCl_2 \text{ (anhydrous zinc chloride)}$$

$$3Zn + 2NH_3 \xrightarrow{\Delta} Zn_3N_2 + 3H_2\uparrow$$

(7) *Displacement reactions.* Zinc displaces less electropositive metals, *e.g.*, silver, from their salts in aqueous solution.

$$Zn + 2AgNO_3 \rightarrow Zn(NO_3)_2 + 2Ag\downarrow$$

## 36. Uses of Zinc

(1) *For roofing*, because of its resistance to corrosion, and in die casting.

(2) *For making cathode containers* of dry cells.

(3) *In the metallurgy of silver and gold* by the cyanide process and for the desilverization of lead by Parke's process.

(4) *As a reducing agent.* Zinc dust, Zn/HCl, zinc-copper couple, etc. are used as reducing agents in the laboratory and in the manufacture of drugs, dyestuffs, perfumes, etc.

(5) *For making alloys, e.g*, brass, German silver (a white, soft alloy wito high electrical resistance), Babbitt metal (an antifriction alloy), etc. Zinc based alloys are used in die castings, automobiles, and in the fabrication of domestic and office articles.

(6) *For making zinc compounds* of commercial importance.

(7) *For galvanizing iron and steel* to prevent rusting.

**36-1. Galvanizing**. The process of depositing a protective coating of zinc on iron and steel to prevent rusting is called *galvanizing* while the product is known as *galvanized* iron or steel. The protective action of zinc depends upon the formation of a protective film of basic carbonate upon its surface. Furthermore, being a more active metal it corrodes first keeping the less active iron protected.

Before galvanizing, iron or steel is cleaned and freed from grease and tarnish. The metal is first washed with hot alkali solution to remove the grease. The oxide film is removed by 'pickling' in an acid bath (dilute sulphuric or hydrochloric acid). It is then galvanized by one of the following methods :

(*a*) *Hot galvanizing method.* The sheet iron or wire is dipped into molten zinc and then run through hot rollers to remove superfluous zinc. Thus a thin and uniform coating of zinc is obtained.

(*b*) *Electrogalvanizing (cold galvanizing).* This method involves the electro-deposition of zinc on iron The article to be galvanized is made the cathode and zinc rod the anode in a plating bath of acidified sulphate.

(*c*) *Sherardizing*. In this process, the articles are packed in a revolving drum with zinc dust and heated to 400°C for several hours. Under these conditions, the zinc dissolves in the surface of iron, forming a corrosion-resistant alloy. This method is mainly employed for galvanizing articles of intricate shapes *e.g.*, bolts, pulleys, etc.

(*d*) *Metallizing*. This process consists in spraying atomized zinc with great force against iron objects. This results in the formation of a firmly-adherent coating of zinc on the objects.

## COMPOUNDS OF ZINC

## 37. Zinc Oxide, ZnO

*Preparation*. By burning zinc in air when zinc oxide is formed as a dense white smoke.

$$2Zn + O_2 \rightarrow 2ZnO$$

*Properties*. It is a white, loose powder, commonly called *Philosopher's wool*. It dissolves in acids ($H^+$) to give zinc salts ($Zn^{2+}$) and in alkalis ($OH^-$) to give zincates ($ZnO_2^{2-}$). It is therefore, an amphoteric oxide.

$$ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O; \quad ZnO + 2OH^- \rightarrow ZnO_2^{2-} + H_2O$$

*Uses*. (1) It is used *as a white paint pigment* under the name *zinc white*. It gives the truest white colour unaffected by $H_2S$.

(2) On account of its toxicity, it is used *as an antiseptic* in white medical adhesive tapes and in skin ointments.

(3) It is also used *as a filler* in automobile tyres.

(4) It is used in making oil cloth, certain types af glazes, enamels, and special types of glass.

## 38. Zinc Chloride, $ZnCl_2$

*Preparation*. It is prepared by dissolving zinc, its oxide, hydroxide, or carbonate in hydrochloric acid. The solution on evaporation in presence of excess acid deposits crystals of the mono-hydrate, $ZnCl_2.H_2O$. In the absence of free acid, however, basic salts, $Zn(OH)Cl$ and $Zn_2OCl_2$, are formed due to hydrolysis.

**Anhydrous zinc chloride** is obtained (*i*) By heating zinc in a stream of chlorine or dry hydrogen chloride.

(*ii*) By distilling zinc with mercuric chloride.

$$Zn + HgCl_2 \rightarrow ZnCl_2 + Hg\uparrow$$

(*iii*) By heating the double salt $ZnCl_2.3NH_4Cl$ in a current of dry hydrogen chloride.

*Properties*. (1) Anhydrous zinc chloride is a very deliquescent white solid. It dissolves in water exothermically giving an acidic solution due to hydrolysis.

$$ZnCl_2 + H_2O \leftrightharpoons Zn(OH)Cl + HCl$$

(2) It is also soluble in alcohol, ether and, acetone. This property, as also the low conductivity of molten zinc chloride, point towards its partly covalent character.

(3) On heating the hydrated salt, oxychloride is first formed which yields the oxide on strong heating.

$$\mathrm{ZnCl_2.H_2O \rightarrow ZnCl_2 + H_2O}$$

$$\mathrm{ZnCl_2 + H_2O \rightarrow Zn(OH)Cl + HCl\uparrow}$$

$$\mathrm{Zn(OH)Cl \rightarrow ZnO + HCl\uparrow}$$

*Uses.* (1) Anhydrous zinc chloride is used *as a dehydrating agent* in organic chemistry. (2) *As a flux in soldering* to remove oxide films from metal surfaces, owing to the acidic nature of moist $ZnCl_2$. (3) *As a wood preservative* since, being toxic, it destroys termites and other injurious insects. (4) Mixed with moist zinc oxide it gives a hard mass of zinc hydroxychloride, Zn(OH)Cl, used for filling teeth *in dentistry*. (5) *In the manufacture of fibreboard* which is a gelatinous mass produced by the action of concentrated solution of zinc chloride on cellulose. It can be moulded into any shape and is used in making boxes, trays, insulating material, etc.

## 39. Zinc Sulphate, White Vitriol, $ZnSO_4.7H_2O$

*Preparation.* It may be prepared by concentrating a solution of zinc, its oxide, or carbonate in dilute sulphuric acid and cooling the solution below 40°.

*Properties.* It is a white crystalline substance very soluble in water. It is isomorphous with the heptahydrated sulphates of iron nickel, cobalt magnesium, manganese, and cadmium. When heated it changes thus :

$$\begin{tikzcd} \mathrm{ZnSO_4.7H_2O} \arrow[r, "\Delta", "-\mathrm{H_2O}"'] & \mathrm{ZnSO_4.6H_2O} \arrow[r, "100^\circ\mathrm{C}", "-5\mathrm{H_2O}"'] & \mathrm{ZnSO_4.H_2O} \arrow[r, "250^\circ\mathrm{C}", "-\mathrm{H_2O}"'] & \mathrm{ZnSO_4} \arrow[d, "750^\circ\mathrm{C}"] \\ & & & \mathrm{ZnO + SO_3\uparrow} \end{tikzcd}$$

*Uses.* (1) In the preservation of hides, (2) As a mordant, (3) In eye lotions, and (4) In making *lithopone.*

## 40. Zinc Sulphide, ZnS

*Preparation.* It occurs in nature as *zinc blende*. It is the only sulphide among those of ordinary metals which is both white and extremely insoluble. In the laboratory it is prepared by passing hydrogen sulphide through neutral solutions of zinc salts or ammoniacal solutions containing ammonium chloride. It may also be made by heating zinc metal with sulphur.

*Properties.* It is a white substance insoluble in water. It dissolves in mineral acids forming corresponding zinc salts with the liberation of hydrogen sulphide.

$$\mathrm{ZnS + H_2SO_4 \rightarrow ZnSO_4 + H_2S\uparrow}$$

*Uses.* (*i*) It is used as a white pigment, either alone or mixed with zinc oxide. Lithopone, an important white paint pigment, is a mixture of zinc sulphide and barium sulphate. It is precipitated by mixing solutions of zinc sulphate and barium sulphide.

$$BaS + ZnSO_4 \rightarrow BaSO_4\downarrow + ZnS\downarrow$$

(*ii*) Zinc sulphide containing traces of impurities such as manganese or copper is phosphorescent, and is used for the manufacture of luminous paints.

## 41. Zinc Carbonate, $ZnCO_3$

*Preparation.* Zinc carbonate occurs in nature as *calamine*. In the laboratory, it may be prepared by adding an aqueous solution of sodium bicarbonate to the solution of a zinc salt.

$$ZnSO_4 + 2NaHCO_3 \rightarrow ZnCO_3\downarrow + Na_2SO_4 + H_2O + CO_2\uparrow$$

$$Zn^{2+} + 2HCO_3^- \rightarrow ZnCO_3^-\downarrow + H_2O + CO_2\uparrow$$

Addition of the normal carbonate instead of the bicarbonate results in the precipitation of basic zinc carbonate, $ZnCO_3.2Zn(OH)_2.H_2O$.

*Properties.* It is a white powder which readily decomposes on heating ($ZnCO_3 \rightarrow ZnO + CO_2\uparrow$). It dissolves in acids forming zinc salts (*e.g.*, $ZnCO_3 + 2HCl \rightarrow ZnCl_2 + H_2O + CO_2\uparrow$).

*Uses.* It is used in making cosmetics, *e.g.*, *calamine lotion* (1 g zinc carbonate, 5 ml lime water, 12 ml glycerine, and 30 ml water).

### Questions

1. Account for the following :

(*a*) Transition metals show horizontal similarities in physical and chemical properties.

(*b*) Iron shows valencies of +2 and +3, but zinc is consistently divalent.

(*c*) The $Fe^{2+}$ and $Cu^{2+}$ ions are coloured; $Zn^{2+}$ ion is colourless.

(*d*) Most transition metals are paramagnetic.

2. Write down the electronic configurations of iron, copper, and zinc, and on their basis, explain the valencies exhibited by these elements.

3. (*a*) Describe the extraction of iron from hematite. Give only the reactions that occur.

(*b*) What are the main products of the blast furnace for the extraction of iron.

4. (*a*) Describe the manufacture of steel by any one process.

(*b*) Write an explanatory note on the heat treatment of steels.

5. Describe the electric furnace for the manufacture of steel. Mention *three* metals used for the manufacture of alloy steels. What is the essential difference between steel and wrought iron ?

6. (*a*) Explain the process of the rusting of iron.

(*b*) Describe briefly the methods for the prevention of rusting.

7. (*a*) Give the preparation, properties, and uses of (*a*) ferrous sulphate, and (*b*) ferric chloride.

(*b*) Give any three tests for distinguishing between iron (II) and iron (III) compounds.

8. (*a*) List the names and formulae of three ores of copper.

(*b*) How is copper extracted from copper pyrites.

(*c*) How is copper refined electrolytically ? Explain the process.

(*d*) List the important uses of copper metal.

9. How is copper sulphate industrially made ? Describe its reactions with alkalis, ammonia, and potassium iodide. What are its important uses ? Draw its structure.

10. (*a*) Mention the names and formulae of the carbonate, oxide, and sulphide ores of zinc.

(*b*) Describe any process for the extraction of zinc from its ores.

(*c*) Give chemical equations for the reactions of zinc with *i.* dilute nitric acid, *ii.* concentrated nitric acid, *iii.* boiling aqueous solution of sodium hydroxide, and *iv.* an aqueous solution of silver nitrate.

(*d*) Mention two important uses of zinc.

11. (*a*) Write an explanatory note on 'galvanizing'.

(*b*) Give the preparation, properties, and uses of any two of the following :

*i.* Zinc oxide
*ii.* Zinc sulphate
*iii.* Zinc chloride
*iv.* Zinc carbonate.

□ □

# 15

# Lanthanides and Actinides

Within the third transition series (elements 57,72-80), there is yet another series of 14 elements (atomic numbers 58-71) called the *rare earths* or lanthanides. They are characterized by the filling of the antepenultimate $4f$ energy level while the outermost shell has 2 electrons ($6s^2$), and the next inner one has 9 electrons ($5s^25p^65d^1$). The $4f$ level begins to be built up with one electron at Ce (58) and becomes complete with 14 electrons at Lu (71). Owing to the identical electron configurations of the two outer shells, all lanthanides are extremely alike. Hence, they are placed in the same space in the periodic table, corresponding to the atomic number 57, which is that of lanthanum.

Corresponding to the lanthanides in the sixth period are the 14 elements following actinium (89) in the seventh period whose atoms build up the $5f$ sublevel. These elements are called the *actinides*. They are all placed in the same space in the periodic table along with actinium (89).

Since in the atoms of the lanthanides and actinides both the electrons are added to the $f$ sublevel of the antepenultimate shell, they are grouped as the *f-block elements*. Owing to their occurrence within the transition series, they are also called the *inner transition* elements.

## I. LANTHANIDES (THE CERIUM FAMILY)

## 1. General Features of the Lanthanides

**1. Electronic configuration.** The lanthanides are situated in period 6, their atoms having six electron shells each. The electron configuration of the two outer shells is the same in all the lanthanides—$5s^25p^65d^1$, $6s^2$. Their antepenultimate shell, *i.e.*, the fourth shell has completed $s$, $p$, and $d$ levels while the number of electrons in the $f$-level regularly increases from 1 to 14 as the atomic number increases by one.

**Table 15-1** *Electron configurations of the lanthanides**

| *Element* | *At. No.* | *Electron configuration* |
|---|---|---|
| Ce | 58 | $1s^2\ 2s^22p^6\ 3s^23p^63d^{10}\ 4s^24p^64d^{10}\ 4f^1\ 5s^25p^65d^1\ 6s^2$ |
| Pr | 59 | $4f^2\ 5s^25p^65d^1\ 6s^2$ |
| Nd | 60 | $4f^3\ 5s^25p^65d^1\ 6s^2$ |
| Pm | 61 | $4f^4\ 5s^25p^65d^1\ 6s^2$ |
| Sm | 62 | $4f^5\ 5s^25p^65d^1\ 6s^2$ |
| Eu | 63 | $4f^6\ 5s^25p^65d^1\ 6s^2$ |
| Gd | 64 | $4f^7\ 5s^25p^65d^1\ 6s^2$ |
| Tb | 65 | $4f^8\ 5s^25p^65d^1\ 6s^2$ |
| Dy | 66 | $4f^9\ 5s^25p^65d^1\ 6s^2$ |
| Ho | 67 | $4f^{10}\ 5s^25p^65d^1\ 6s^2$ |
| Er | 68 | $4f^{11}\ 5s^25p^65d^1\ 6s^2$ |
| Tm | 69 | $4f^{12}\ 5s^25p^65d^1\ 6s^2$ |
| Yb | 70 | $4f^{13}\ 5s^25p^65d^1\ 6s^2$ |
| Lu | 71 | $4f^{14}\ 5s^25p^65d^1\ 6s^2$ |

**2. Valency and type of bonding.** The usual valency of the lanthanides is +3 which is shown by all members The sum of their first three ionization energies being quite low, they form $M^{3+}$ ion, which dominates their chemistry. The trivalent metal ion, $M^{3+}$, is formed by utilizing the two 6*s* electrons and one 5*d* electron. Many trivalent lanthanide ions are strikingly coloured both in the solid state and in aqueous solution. Some of the lanthanides have anomalous valencies of +2 and +4. However, the $M^{2+}$ and $M^{4+}$ ions that do occur are always less stable than $M^{3+}$ ion.

**3. Physical Properties.** The lanthanides are high-melting, silvery-white, lustrous metals. They are ductile, are of relatively low hardness, and are close to mercury in electrical conductivity.

**4. Chemical properties.** The lanthanides, along with lanthanum, come after the alkali and alkaline earth metals. They are all electro-positive and quite reactive, comparing with magnesium in reactivity.

(*i*) *Action of air.* Though quite stable in dry air, the lanthanides rapidly tarnish in moist air. When heated to 200°−400°C they ignite in air and burn, forming mixtures of their oxides and nitrides. Powdered cerium is pyrophoric, *i.e.*, ignites spontaneously in air in normal conditions.

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*The names of the lanthanides from 58 to 71 are Cerium, Praseodymium, Neodymium, Promethium, Samarium, Europium, Gadolinium. Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium, and Lutetium. It may be noted that the electron configurations of the lanthanide elements are not known for certain. Alternative electronic structures involve moving the single 5*d* electron into the 4*f* level, except where this disturbs a half full *f* shell. According to this pattern, cerium has the configuration $4s^24p^64d^{10}4f^2$, $5s^25p^6$, $6s^2$.

(*ii*) *Action of water and acids.* The lanthanides react slowly with cold water, and rapidly on heating forming their hydroxides with the liberation of hydrogen.

$$2M + 6H_2O \rightarrow 2M(OH)_3 + 3H_2\uparrow; \quad M = \text{a lanthanide}$$

They react even more energetically with acids, liberating hydrogen and forming their corresponding salts. However, they are stable in HF and $H_3PO_4$, since a protective film of insoluble salt is formed on their surface.

Lanthanides do not react with alkalis.

(*iii*) *Combination with hydrogen.* The metals combines with hydrogen at 300°—400°C forming their hydrides. These hydrides are partially ionic and react with water liberating hydrogen.

$$\underset{\text{ceric hydride}}{CeH_3} + 3H_2O \dashrightarrow \underset{\text{ceric hydroxide}}{Ce(OH)_3} + 3H_2\uparrow$$

(*iv*) *Combination with halogens and other non-metals.* Lanthanides combine with halogens on heating to give the anhydrous halides $MX_3$. They also react, when heated, with nitrogen, sulphur, phosphorus, carbon, silicon, etc.

(*v*) *Alloy formation.* Lanthanides alloy with most metals, and often form intermetallic compounds, *e.g.*, CeAl, $Ce_3Al$, CeMg, $CeMg_3$, $CeCu_2$, etc.

**5. Compounds.** Being chemically reactive, the lanthanides form numerous compounds—oxides, hydroxides, halides, nitrates, carbonates, sulphates, phosphates, etc. Their *oxides*, $M_2O_3$ are ionic and basic, and are very refractory (m. p. of the order of 2000°C). They are practically insoluble in water, but react with it to form hydroxides, liberating heat. Their *hydroxides*, $M(OH)_3$, are also ionic and basic. They absorb carbon dioxide from air and form carbonates. The basic character of both the oxides and hydroxides decreases with the decreasing ionic radius in the $Ce^{3+}-Lu^{3+}$ series.

The trivalent chlorides, nitrates, and sulphates of lanthanides are soluble in water and hydrolyse but very slightly; their carbonates, sulphides, fluorides, phosphates, oxalates, etc., are almost insoluble.

## 3. Lanthanide contraction

Normally the atomic size increases on moving down a group in the periodic table as extra shells of electrons are added. On moving across a period, the atomic size decreases because the nuclear charge is increased and since the extra orbital electrons shield the charge imperfectly, all the electrons are pulled inward. In the lanthanide series the electron is added to an inner shell and this would be expected to completely offset the effect of the increased nuclear charge. However, the shielding effect of *f* electrons is very weak owing to the shape of the *f* orbitals being highly diffused. As such the atomic size, covalent radii, and the ionic radii in the series $Ce^{3+}-Lu^{3+}$ gradually decrease in the lanthanide series with increases in atomic number.

The small but steady decrease in the atomic and ionic radii of lanthanides is called **lanthanide contraction**. It influences the chemistry of not only the lanthanides but also of the elements (numbered 72-80) which follow them in the transitions series of the sixth period. The more important consequences of lanthanide contraction are :

1. There is a very small but steady increase in the standard electrode potential value, $E^0$, for the process $M^{3+} + 3e^- \rightarrow M(g)$ from Ce to **Lu**.

2. There is a decrease in the basic strength of the oxides and hydroxides of lanthanides with increase in atomic number. $Ce(OH)_3$ is the most basic, $Lu(OH)_3$ is the least. The reason is that the decrease in the size of the $M^{3+}$ ion increases the covalent character between the $M^{3+}$ ion and $OH^-$ ion (according to Fajan's rules), so that the degree of dissociation of the lanthanide hydroxide is decreased.

3. The transition elements (numbered 72-80) following the lanthanides have almost the same atomic size as the vertically preceding element in their respective groups as given in Table 15-2.

**Table 15-2** *Atomic radii of elements preceding and following lanthanides*

| III B | | IVB | VB | VIB | VIIB | VIII | | | IB | IIB |
|---|---|---|---|---|---|---|---|---|---|---|
| $Sc_{21}$<br>1·44 | | $Ti_{22}$<br>1·32 | Y<br>1·18 | Cr<br>1·18 | Mu<br>1·17 | Fe<br>1·17 | Co<br>1·16 | Ni<br>1·15 | Cu<br>1·17 | $Zn_{30}$<br>1·25 |
| $Y_{89}$<br>1·62 | | $Zr_{40}$<br>1·45 | Nb<br>1·35 | Mo<br>1·30 | Tc<br>1 27 | Ru<br>1 25 | Rh<br>1·25 | Pd<br>1·28 | Ag<br>1·34 | $Cd_{48}$<br>1·48 |
| $La_{57}$<br>1·69 | $Ce_{58}-Lu_{71}$<br>1·65 1·56<br>14 lanthanides | $Hf_{72}$<br>1·44 | Ta<br>1·34 | W<br>1·30 | Re<br>1·28 | Os<br>1·26 | S<br>1 26 | Pt<br>1·30 | Au<br>1·34 | $Hg_{80}$<br>1·49 |

Thus Zr and Hf of Group IVB have nearly the same atomic radii, though normally there would be a big increase in the atomic radius of Hf as is the general trend in moving down a group in the periodic table. The lanthanide contraction almost balances the expected increase in the atomic sizes of the elements of Groups IVB through IIB in the fifth and sixth periods of the periodic table.

## 4. Occurrence and Isolation of Lanthanides

**4-1. Occurrence.** In nature the abundance of lanthanides is comparable to that of copper, antimony, and iodine. They are found in many rare minerals which exist in a few widely separated localities. More than 250 minerals containing them are known. They occur usually in intimate association with one another and with zirconium hafnium, and thorium of Group IVB. The most important source of lanthanides is the mineral *monazite* (also called *monazite sand*) found along the seacoast in India (Malabar coast), Brazil, and Carolinas. It contains the various lanthanide metals as their phosphates, mainly cerium phosphate, $CePO_4$, along with 5-9 per cent thoria ($ThO_2$) and traces of uranium.

**4-2. Isolation**. The isolation of the separate lanthanides from monazite is a difficult problem owing to the great similarity in their properties. Formerly, the only effective method of separation was that of fractional crystallization of certain of their salts. This involved hundreds (even thousands) of operations of precipitation and recrystallization. Recently ion exchange methods which provide a much more rapid and effective separation have been used. The method consists in the *selective adsorption* of the ions of the various lanthanide ions on a column of synthetic ion exchange resin which has such functional groups as $-COOH$ or $-SO_3H$ This is followed by fractional dissolution of the adsorbed material in a suitable solvent.

Once the compounds of the different lanthanide elements have been separated, the metals are obtained by electrolysis of their molten chlorides or by reducing the trichlorides or trifluorides with calcium at 1000°C in an argon-filled vessel.

## 5. Uses of Lanthanides and Their Compounds

The lanthanide metals and their compounds find more and more applications in technology over the years. Some of the main applications are as follows :

1. Because of their extraordinary capacity to combine with many gases, they are used *in vacuum technology*.

2. They are used *in steel-making* as alloying admixtures to improve the mechanical properties of alloys.

3. *Metallic cerium* is used as an admixture *in magnesium and aluminium alloys* to increase mechanical strength.

4. An alloy of iron with 70 percent cerium and smaller amounts of other lanthanides, called *misch metal*' is pyrophoric. It is used to make flints for cigarette lighters, tracer bullets, etc., as when subjected to friction they give off sparks.

5. The metals and their compounds are good *catalysts* in many organic and inorganic syntheses.

6. Lanthanide oxides are used *for polishing glass*; cerium salts are sometimes used to colour glass and porcelain. Lanthanide compounds are also used to produce special grades of glass.

7. Cerium dioxide (about 2 per cent) mixed with thorium oxide (about 88 per cent) is used in the manufacture of incandescent gas mantles.

8. Because of their high melting points the oxides, carbides, nitrides, and sulphides of lanthanides are used *in making refractory ceramics*.

## II. ACTINIDES (THE THORIUM FAMILY)

### 6. General Features of the Actinides

1. **Electronic configuration.** The actinides are analogous to the lanthanides in that the electron configurations of succeeding elements (numbered 90 to 103) in the series differ by one electron in the $5f$ or $6d$ sublevels. Their electronic structures are given in Table 15-3.

Table 15-3 *Electronic configurations of actinides*

| Element | Symbol | At. No. | Electronic configuration |
|---|---|---|---|
| Thorium | Th | 90 | Radon core—$5f^0$ $6d^2$ $7s^2$ |
| Protoactinium | Pa | 91 | $5f^1$ $6d^2$ $7s^2$ |
| Uranium | U | 92 | $5f^3$ $6d^1$ $7s^2$ |
| Neptunium | Np | 93 | $5f^5$ $6d^0$ $7s^2$ |
| Plutonium | Pu | 94 | $5f^6$ $6d^0$ $7s^2$ |
| Americium | Am | 95 | $5f^7$ $6d^0$ $7s^2$ |
| Curium | Cm | 96 | $5f^7$ $6d^1$ $7s^2$ |
| Berkelium | Bk | 97 | $5f^8$ $6d^1$ $7s^2$ |
| Californium | Cf | 98 | $5f^{10}$ $6d^0$ $7s^2$ |
| Einsteinium | Es | 99 | $5f^{11}$ $6d^0$ $7s^2$ |
| Fermium | Fm | 100 | $5f^{12}$ $6d^0$ $7s^2$ |
| Mendelevium | Md | 101 | $5f^{13}$ $6d^0$ $7s^2$ |
| Nobelium | No | 102 | $5f^{14}$ $6d^0$ $7s^2$ |
| Lawrencium | Lr | 103 | $5f^{14}$ $6d^1$ $7s^2$ |

It is clear from Table 15-3 that the electronic configurations of actinides show more frequent irregularities than those of lanthanides.

2. **Valency and type of bonding.** The actinides have a characteristic valency of +3, but show a much wider variation in valencies than do the lanthanide elements. For the elements Th, Pa, and U, the most stable valencies are +4, +5, and +6. Compounds in the +3 valence state are ionic, those in higher valence states are covalent.

3. **Physical properties.** The elements are all silvery-white metals with high density (of the order of $11-20$ g/cm$^3$) and relatively high melting points (640°$-$2000°C).

4. **Atomic size and ionic size.** The size of the atoms as well as ions decreases regularly along the series, because of the poor screening of the nuclear charge by the *f* electrons.

5. **Chemical properties.** The elements are chemically reactive. When burnt in oxygen, they form oxides, *e.g.*,

$$Th + O_2 \rightarrow ThO_2$$
$$3U + 4O_2 \rightarrow U_3O_8 \ (UO_2.2UO_3)$$

They react readily with many other non-metals, including hydrogen, when heated.

With metals the actinides form alloys containing intermetallic compounds, *e.g.*, $PuAl_2$, $PuFe_2$, etc.

All actinides are radioactive, and their chemical study is often greatly complicated by their rapid radioactive decay.

## 7. Occurrence, Production, and Uses of Actinides

Thorium, protoactinium, and uranium occur on earth. Other actinides do not occur in nature (except minute quantities of neptunium and plutonium). They are prepared by nuclear reactions and only exist as radioactive isotopes which are not very stable. The most important elements in the series are thorium, uranium, and plutonium, their importance being largely related to their use in the development of atomic energy.

**7·1. Thorium.** *Occurrence.* Thorium occurs up to 30 per cent in monazite sand, mixed with the phosphates of lanthanides. Indian monazite has as high as 10 per cent of thoria (thorium dioxide), $ThO_2$.

*Production.* Metallic thorium is produced by reducing the tetrachloride, $ThCl_4$, with sodium; the thorium tetrachloride is obtained by heating a mixture of thorium dioxide and carbon in a current of chlorine.

$$ThO_2 + 2C + 2Cl_2 \xrightarrow{\Delta} ThCl_4 + 2CO\uparrow$$

$$ThCl_4 + 4\,Na \xrightarrow{Na} Th + 4NaCl$$

*Uses.* (1) *As a component of heat-resistant alloys.*

(2) *In the production of fissionable* $^{233}_{92}U$. Naturally occurring thorium is almost entirely $^{232}Th$, which is not fissionable. When it is irradiated in the outer part of a nuclear reactor, $^{233}U$ is formed

$$^{232}_{90}Th \xrightarrow{+n/\gamma} {}^{233}_{90}Th \xrightarrow[22\ \text{min.}]{-\beta} {}^{233}_{91}Pa \xrightarrow[27\ \text{days}]{-\beta} {}^{233}_{92}U\ ,$$

This isotope of uranium is fissionable and has a half life of $1{\cdot}6 \times 10^5$ years. It does not occur in nature.

(3) *In incandescent gas mantles.* Thorium dioxide mixed with 1 per cent of cerium dioxide gives off brilliant white light when heated, hence it is used for making incandescent gas mantles. The mantle woven from silk fibres is dipped in a solution containing thorium nitrate together with about 1 per cent of cerium nitrate, dried, and fixed in the lamp. When ignited the first time, the silk fibres burn away leaving behind a net-work of infusible $ThO_2$ and $CeO_2$ formed by the decomposition of the nitrates.

**7-2. Uranium.** *Occurrence* The most important mineral and ore of uranium is pitchblende, $U_3O_8$ mined in Zaire, Canada, and the U.S.A. It is interesting to note that the element is more abundant than many 'well known' elements, such as Ag, Cd, Hg, and I.

*Production.* The extraction processes are complex and involve, in the final step, the reduction of the fluoride, $UF_4$, or the oxide, $UO_2$, with calcium or magnesium.

*Uses.* (1) In the production of nuclear energy.

(2) Uranium compounds are used for producing yellow glazes on ceramic ware, as mordants, and in the dye industry.

**7-3. Plutonium.** *Occurrence.* Plutonium, along with uranium, actinium, protoactinium, and neptunium, occurs in traces in pitchblende.

*Production.* Plutonium is produced in atomic reactors from uranium-238.

$$\begin{array}{ccccccccc} {}^{238}_{92}\mathrm{U} & + & {}^{1}_{0}n & \longrightarrow & {}^{239}_{92}\mathrm{U} & \xrightarrow{-\beta} & {}^{239}_{93}\mathrm{Np} & \xrightarrow{-\beta} & {}^{239}_{94}\mathrm{Pu} \\ \text{stable} & & & & \text{unstable} & & \text{unstable} & & \text{stable} \\ t_{1/2} = 4{\cdot}5\times 10^{9}\text{ years} & & & & 25\text{ min} & & 2{\cdot}33\text{ days} & & 2{\cdot}4\times 10^{4}\text{ years} \end{array}$$

*Use.* Plutonium is fissionable and is used as a fuel in atomic energy plants.

## Questions

1. (*a*) Why are the lanthanides and actinides called *f*-block elements? Why do the members of each series number 14 ?

(*b*) What is the number of electrons in the outermost electron shell of the lanthanide and actinides ?

(*c*) Why are the lanthanides extremely alike in chemical properties ?

(*d*) What is the most characteristic valency of the lanthanides ? Of actinides ?

(*e*) Write a balanced chemical equation for the reaction of cerium with water.

2. Explain the reason why the basic character of the hydroxides of lanthanides, $M(OH)_3$, decreases gradually in the series Ce—Lu.

3. What do you understand by the term 'lanthanide contraction' ? What are the important consequences of this phenomenon ?

4. (*a*) Name the principle source of the lanthanides ?

(*b*) Outline the ion-exchange method for the separation of lanthanides.

(*c*) Give three main uses of lanthanide elements.

5. (*a*) Name the chief ore of uranium.

(*b*) Describe, mainly by means of chemical equations, the production of any one of the elements thorium, uranium, and plutonium.

(*c*) Give the main uses of thorium.

## Key

1. (*a*) The difference in the electron configurations of the lanthanide elements is exclusively in the antepenultimate shell, which does not affect their chemical properties.

(*b*) $2Ce + 6H_2O \rightarrow 2Ce(OH)_3 + 3H_2\uparrow$

2. As the atomic and ionic radii increase from Ce to Lu, the bond between $M^{3+}$ and $OH^-$ becomes increasingly covalent and the degree of dissociation of the hydroxides correspondingly decreases.

# 16

# The Noble Gases

The noble gases are the elements ending each period in the periodic table; all together, they constitute the *zero group*. They are, in the order of increasing atomic numbers, helium (He), neon (Ne), Argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn). These gaseous elements have little tendency to react with anything else. For this reason, they were originally called the **inert gases**. It is now known that they do form compounds under the proper conditions. For this reason they are now called the **noble gases**, rather than the inert gases. The term *noble gas* implies that these elements tend to exist by themselves, and not in the company of other elements. Because of their occurrence on earth in very minute amounts, these elements are also called the *rare gases*.

It is interesting to note that the inert nature of the noble gases is not a handicap; it makes possible a number of important applications.

## 1. Discovery of Noble Gases

The noble gases were discovered towards the end of the 19th century. The history of their discovery may be traced stepwise as follows :

(*a*) In 1892 Lord Rayleigh found that nitrogen prepared from the air by removing all other gases always had about 0·5 per cent higher density than the nitrogen prepared from its compounds (*e.g.*, by heating ammonium nitrite). This suggested the presence of some yet undiscovered heavier gas in the air. To verify this, Ramsay repeatedly passed nitrogen prepared from the air over heated magnesium (which combines with nitrogen to form $Mg_3N_2$). He found that a small fraction (1·2 per cent by volume) was left unchanged. This gas was found to be considerably denser than nitrogen. Its presence in small amounts was sufficient to account for the above mentioned difference in density. This gas was named 'argon', meaning 'the lazy one' as it would not combine with any other element. It was initially regarded as a single element but was later found to be a mixture of helium, neon, argon, krypton, and xenon.

(*b*) **Helium** was first detected spectroscopically in 1868 in the atmosphere surrounding the sun (therefore the name helium, from the Greek word 'helios', meaning the sun). In 1895, Ramsay established the existence of helium on earth when he obtained it by heating the uranium mineral clevite with sulphuric acid.

(*c*) In 1898 Ramsay and Travers isolated **neon** (meaning 'the new element') **krypton**, ('the hidden element') and **xenon** ('the stranger') by the fractional distillation of the main fractions of liquid air.

(*d*) In 1900 Dorn discovered **radon**, the heaviest noble gas, among the disintegration products of radium.

## 2. Electronic Configurations of Noble Gases

Helium has only two electrons in its first shell, which is also the outermost shell for it in the ground state. Other noble gases have a completely filled set of *s* and *p* orbitals in their outermost shell. That is, the electronic configuration for the outermost shell is $s^2p^6$ in each case.

**Table 16-1** *Electronic configurations of noble gases*

| *Element* | *Symbol* | *At. No.* | *Electronic Configuration* |
|---|---|---|---|
| Helium | He | 2 | $1s^2$ |
| Neon | Ne | 10 | $1s^2, 2s^2\ 2p^6$ |
| Argon | Ar | 18 | $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6$ |
| Krypton | Kr | 36 | $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^6$ |
| Xenon | Xe | 54 | $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^6\ 4d^{10}, 5s^2\ 5p^6$ |
| Radon | Rn | 86 | $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}, 5s^2\ 5p^6\ 5d^{10}, 6s^2\ 6p^6$ |

The $s^2p^6$ configuration of the outermost shell is apparently a very stable electron configuration. In many compounds, the atoms attain this configuration, called the *noble gas configuration.*

## 3. Noble Gases in Nature

The noble gases always occur in the free state. Except the radioactively unstable radon, all of them occur in the atmosphere, collectively constituting 1% of it by volume. These gases in the order of abundance in air are : argon (934 ppm*), neon (1·82 ppm), helium (0·524 ppm), krypton (0·114 ppm), and xenon (0·0097 ppm).

Helium, neon, and argon are also found dissolved in small amounts in certain natural spring waters.

Helium is present up to 6 per cent by volume in the natural gases which issue from the ground in the United States. It occurs in the minerals of uranium and thorium, being formed during the radioactive decay of these elements. Immense amounts of helium are present on stars where it is produced by the thermonuclear fusion of hydrogen atoms into helium with release of energy.

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*Parts per million.

## 4. Isolation of Noble Gases

**4-1. From air.** The noble gases (except radon) are produced by the fractional distillation of liquid air. Where the boiling points are so close together that complete separation is not achieved, use is made of their selective adsorption by charcoal at different low temperatures. At any temperature, the extent of adsorption increases with increasing atomic weight of the noble gas, *i.e.*, in the order He<Ne<Ar<Kr<Xe. Thus, helium and neon isolated as a mixture from liquid air are separated by keeping the gaseous mixture in contact with coconut charcoal at −180°C. The charcoal is contained in a Dewar's bulb surrounded with a cold bath (Fig. 16-1). Neon is completely adsorbed; helium is left unaffected and is pumped out. The adsorbed neon is set free by warming the charcoal.

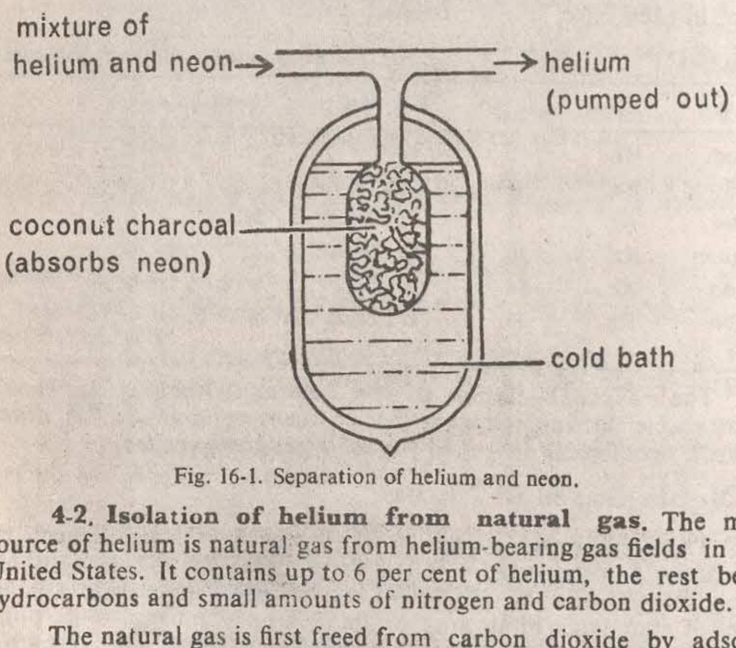


Fig. 16-1. Separation of helium and neon.

**4-2. Isolation of helium from natural gas.** The main source of helium is natural gas from helium-bearing gas fields in the United States. It contains up to 6 per cent of helium, the rest being hydrocarbons and small amounts of nitrogen and carbon dioxide.

The natural gas is first freed from carbon dioxide by adsorption in sodium hydroxide solution under pressure. The remaining gas is cooled progressively to −200°C under pressure. All other gases except helium are liquefied. The residual helium is pumped off. It is purified by passing it over activated charcoal cooled with liquid air, which adsorbs any traces of heavier gases, leaving helium unaffected.

**4-3. Isolation of helium from minerals**. Helium may be isolated from the minerals of uranium and thorium, *e.g.*, clevite, pitchblende, monazite, etc. by heating to about 1000°C in vacuum.

## 5. Physical and Chemical Properties of Noble Gases

**5-1. Physical properties**. The noble gases are all colourless, tasteless, and odourless monatomic gases (*i.e.*, their molecules are single atoms). They are only very slightly soluble in water. Their boiling points and melting points are extremely low in comparison to those of other substances of comparable atomic or molecular weights. This is because no strong chemical bonds, but only weak van der Waal's forces, hold their atoms together in the liquid and solid states.

The boiling points, melting points, densities, solubilities in water, and the atomic radii of the noble gases all regularly increase with increasing atomic number. Helium has the lowest melting point and boiling point of all elements.

**5-2. Chemical properties**. Noble gases are chemically inert. They remain unaffected with acids, alkalis, oxidizing agents, and reducing agents, and do not form compounds. They are so inactive that their atoms do not join together to form diatomic molecules and exist as atoms. Thus, noble gases may be said to be zerovalent. However, a few unstable compound of the noble gases, formed under rather drastic conditions, have been shown to exist, *e.g.*, HgHe, $Hg_2He$, WHe, $Ar.xH_2O$, $Kr.xH_2O$, $Xe.xH_2O$, etc. All of these compounds are extremely unstable and have only a very brief existence.

## 6. Causes of Inertness of the Noble Gases

The great chemical inertness of the noble gases arises from two causes :

1. *Their atoms have electron affinities near to zero.* So, they do not tend to gain electrons from reducing agents.

2. *Their ionization energies are higher than those of any other element.* Thus, they do not tend to lose electrons to oxidizing agents.

## 7. Atomic Weights of Noble Gases

Because the noble gases are chemically inert, it is not possible to determine their atomic weights by chemical methods. Their molecular weights, however, can be calculated from their experimentally determined vapour densities (molecular weight=2 × vapour density). Since the molecules of the noble gases consist of single atoms, their molecular weights are the same as their atomic weights. The atomic weights of helium, neon, argon, krypton, xenon, and radon, thus determined, are 4·00, 20·18, 39·95, 83·80, 131·50, and 222 respectively.

## 8. Uses of Helium and Neon

**8-1. Uses of helium**. *For filling weather observation balloons and airships* in place of hydrogen, since it is not inflammable, does not support combustion, and has a lifting power only 8 per cent less than that of hydrogen.

(2) *For deep-sea breathing*. Deep-sea divers working in special pressurized suits under high pressures use a mixture of oxygen and helium for breathing. If air is used, its nitrogen dissolves in the blood under high pressure when the diver is under deep sea. As he comes to the surface, the pressure is suddenly decreased and the solubility of nitrogen in the blood rapidly decreases (*Henry's law*). The dissolved nitrogen tends to escape forming bubbles in the blood which block its circulation and cause painful 'bends'. Helium is much less soluble in the blood than nitrogen, and diffuses out rapidly through the lungs.

Helium-oxygen mixtures are also used in the treatment of asthma. The lightness and rapid diffussion of helium decreases the muscular effort involved in breathing.

3. *As an inert atmosphere* for the melting and welding of metals and alloys which react with oxygen and nitrogen at high temperatures *e.g.* aluminium and magnesium.

4. *In low temperature research* since rapid evaporation of liquid helium produces temperatures very close to absolute zero. It is also used in thermometers used for low temperature measurements.

**8-2. Uses of neon**. 1. *In neon lamps and neon signs* used for advertising purposes. Neon is filled in tubes etc., at 2 mm pressure. When an electric current is passed through neon at this low pressure, a brilliant orange-red glow is produced which is visible through mist and fog. Glow of different colours can be produced by adding other inert gases, mercury vapour, etc.. to neon, and by using tubes made of glasses of special compositions.

2. *In electric equipment* such as voltage stabilizers, time switches, rectifiers, etc.

### Questions

1. (*a*) Why are the 'noble gases' so called ?

(*b*) What is the atomicity of the noble gases ?

(*c*) Which of the noble gases has the lowest boiling point and melting point ?

(*d*) What is meant by the term 'noble gas configuration' ?

(*e*) Which of the noble gases is most abundant in the atmosphere ?

2. How are helium and neon isolated from air ?

3. Outline the isolation of helium from natural gas.

4. (*a*) Describe the physical properties of the noble gases.

(*b*) Explain the causes of the chemical inertness of the noble gases.

(*c*) How would you determines the atomic weight of neon ?

5. Describe the main uses of helium and neon.

## Key

1. (*b*) One (*c*) Helium (*d*) $s^2p^6$ configuration of the outermost shell in the atom. (*e*) Argon.

4. (*c*) By experimentally determining the vapour density of neon. The vapour density multiplied by 2 will give the molecular weight which, neon being monatomic, will also be the atomic weight.

# 17

# Complex Compounds

An aqueous solution containing equivalent amounts of potassium sulphate and aluminium sulphate yields crystals of potash alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, upon crystallization. Aqueous solutions of potash alum give the reactions for $K^+$, $Al^{3+}$, and $SO_4^{2-}$ ions. Such compounds as potash alum, which give the reactions of the ions of their constituent salts are called double salts. The double salts exist only in the solid state.

When ferrous cyanide dissolves in potassium cyanide solution, crystals having the composition $Fe(CN)_2.4KCN$ can be isolated from the resulting solution. Aqueous solutions of this compound, called potassium ferrocyanide, do not form $Fe^{2+}$ and $CN^-$ ions, but instead give a more complicated structure—the ferrocyanide ion, $[Fe(CN)_6]^{4-}$. This ion takes part in many chemical reactions as a single entity. Ions of this type are called *complex ions*, and the corresponding compounds are called *complex compounds* or coordination compounds. They exist in the solid state as well as in solutions.

## 1. Complex Compounds

Compounds in which a component ion of the molecule, positive, or negative, is made up of a *central atom* surrounded by ions or molecules called *ligands* are called complex compounds, while such an ion is called a complex ion. For example, in the complex compound potassium ferrocyanide, $K_4[Fe(CN)_6]$, the complex ion is $[Fe(CN)_6]^{4-}$ made up of the central atom Fe and six $CN^-$ ligands.

The ligands are attached to the central atom by coordinate bonds, the ligands being the donors and the central atom the acceptor. Hence the name *coordination compounds* for the resulting compounds. There is some question about the theory of coordinate bonding, however, and a more recent theory considers the bond to be an electrostatic attraction between the positively charged central atom and the outermost electrons of ligands. Therefore, the name coordination compound is not very correct, and the more widely used term is complex compounds, or simply *complexes*. In the formulae of complexes, the ligands are shown attached to the central atom by coordinates bonds.

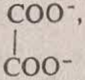
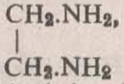
**1-1. The central atom.** The central atoms in complexes are most usually those of the transition metals. The ions of transition metals have vacant *d* orbitals of the right energy which can accommodate electron pairs donated by ligands. Usually, these ions have a high *charge density, i.e.*, small size and high charge (an exception is $Ag^+$ ion). The higher valency ions, *e.g.*, $Fe^{3+}$, $Co^{3+}$, $Cu^{2+}$, etc., form more complexes than the lower valency ion of the same atom, *e.g.*, $Fe^{2+}$, $Co^{2+}$, $Cu^+$, etc. The IA and IIA metal ions do not tend to form complexes since they have lower charge densities due to their relatively large size.

**1-2. Ligands**. Nonmetal atoms with high electronegativities tend to form good ligands if they exist as elementary ions, in polyatomic anions, or in molecules, with a lone pair of electrons. Due to the presence of the lone pair of electrons, the species that act as ligands are always ions or polar molecules. Some common examples of ligands are—

(1) Elementary ions : $F^-$, $Cl^-$, $Br^-$, $I^-$

(2) Polyatomic ions : $OH^-$, $CN^-$, $NO_2^-$, $C_2O_4^{2-}$ (oxalate ion)

(3) Neutral molecules : $H_2O$, $NO$, $NH_3$, $R.NH_2$ (primary amines).

Some ligands have more than one position that can form a bond with the central atom. For example, each of the end oxygen atom in the oxalate ion,  $\begin{array}{c}COO^-\\ |\\ COO^-\end{array}$, can form a bond. Similarly, each of the nitrogen atom in ethylene diamine,  $\begin{array}{c}CH_2.NH_2\\ |\\ CH_2.NH_2\end{array}$, can form a bond. Such ligands as the oxalate ion and ethylenediamine are called *polydentate* ligands or, more specifically bidentate, tridentate, etc. The bidentates are quite common. The ligands having only one point of attachment are referred to as *monodentate*.

## 2. Coordination Number

The coordination number of a central atom (metallic ion) in a complex is equal to the number of coordinate bonds formed around it by the ligands. If each of the ligand forms one bond with the central atom, the coordination number is equal to the number of ligands. In general, the coordination number is of such a value that permits a symmetrical distribution of the ligands around the central atom. The most common coordination numbers are 2, 4 and 6. The coordination number is determined chiefly by the size, electron configuration, and other properties of the central positive ion. Very often, the coordination is equal to twice the charge units on the central ion of the complex.

To write the formula of a complexion, it is necessary to know the valence (*i.e.*, the charge) on the central atom and the ligands, as well as the coordination number of the central atom. The charge on a complex ion is the algebraic sum of the charges on the central atoms and the ligands. For example, the ferrocyanide ion formed from $Fe^{2+}$ and six $CN^-$ ligands, has a charge of $-4$ being the algebraic sum of $+2$ charges from $Fe^{2+}$ and $-6$ charges from the six $CN^-$ ions.

$$Fe^{2+} + 6CN^- \rightarrow [Fe(CN)_6]^{4-}$$

It is conventional to enclose the formula of the complex ion in square brackets.

The formation of the ferrocyanide ion can be shown as follows :

$$Fe^{2+} + 6CN^-: \rightarrow \left[\begin{array}{ccccc} CN: & \searrow & & \swarrow & :NC \\ CN: & \rightarrow & Fe & \leftarrow & :NC \\ CN: & \nearrow & & \nwarrow & :NC \end{array}\right]^{4-} \text{ or } [Fe(CN)_6]^{4-}$$

A few more examples of the formation of complex ions are given below :

(1) *Ferricyanide ion* by the coordination of six $CN^-$ ions with the central $Fe^{3+}$ ion.

$$Fe^{3+} + 6CN:^- \rightarrow \left[\begin{array}{ccccc} CN: & \searrow & & \swarrow & :NC \\ CN: & \rightarrow & Fe & \leftarrow & :NC \\ CN: & \nearrow & & \nwarrow & :NC \end{array}\right]^{3-} \text{ or } [Fe(CN)_6]^{3-}$$

(2) *Hexachloroplatinate ion* by the coordination of six $Cl^-$ ions with the central $Pt^{4+}$ ion.

$$Pt^{4+} + 6\left[:\overset{..}{\underset{..}{Cl}}:\right]^- \rightarrow \left[\begin{array}{ccccc} Cl: & \searrow & & \swarrow & :Cl \\ Cl: & \rightarrow & Pt & \leftarrow & :Cl \\ Cl: & \nearrow & & \nwarrow & :Cl \end{array}\right]^{2-} \text{ or } [PtCl_6]^{2-}$$

(3) *Nickel hexahydrate ion* by the coordination of six water molecules with the central $Ni^{2+}$ + ion.

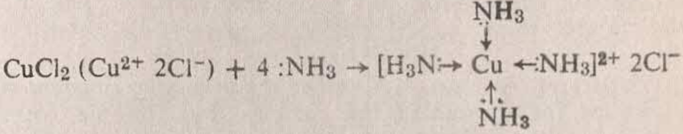
$$Ni^{2+} + 6H_2O: \rightarrow \left[\begin{array}{ccccc} H_2O & \searrow & & \swarrow & OH_2 \\ H_2O & \rightarrow & Ni & \leftarrow & OH_2 \\ H_2O & \nearrow & & \nwarrow & OH_2 \end{array}\right]^{2+} \text{ or } [Ni(H_2O)_6]^{2+}$$

In the formulae of complex compounds, the simple ion attached to the central ion is shown outside the complex—to the left if the complex ion is an anion, to the right if the complex ion is a cation. For example, the formulae of complex compounds corresponding to the complex ions in the above three examples are $K_3[Fe(CN)_6]$, $H_2[Pt\ Cl_6]$, and $[Ni(H_2O)_6]Cl_2$.

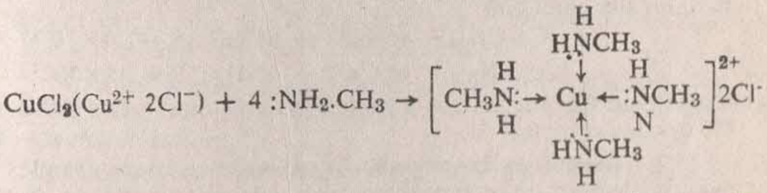
## 3. Coordination of Neutral Ligands

The most important neutral ligands are water and ammonia, the complexes formed by these ligands being called *aquocomplexes*, *e.g.* $[Cr(H_2O)_6]Cl_3$, and *ammoniates*, *e.g.*, $[Co(NH_3)_6]Cl_3$. The water molecules coordinate due to the presence of the lone pair of electrons on the oxygen atom; ammonia and the amines coordinate due to the presence of the lone pair of electrons on the nitrogen atom.

**3-1. Coordination of ammonia and amines with metals.** The ions of transition metals readily accept the unshared pair of electrons on the nitrogen atoms in ammonia and primary amines forming similar complexes. For example, cupric chloride yields deep blue soluble complexes with ammonia and methylamine, $CH_3\,NH_2$, as shown below :

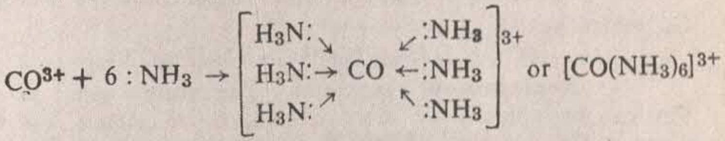


$$CuCl_2\,(Cu^{2+}\,2Cl^-) + 4\,{:}NH_3 \rightarrow [H_3N{:}\rightarrow \underset{\underset{NH_3}{\uparrow}}{\overset{\overset{NH_3}{\downarrow}}{Cu}} \leftarrow{:}NH_3]^{2+}\,2Cl^-$$



$$CuCl_2(Cu^{2+}\,2Cl^-) + 4\,{:}NH_2.CH_3 \rightarrow \left[ \overset{H}{\underset{H}{CH_3N{:}}} \rightarrow \underset{\underset{\underset{H}{HNCH_3}}{\uparrow}}{\overset{\overset{\overset{H}{HNCH_3}}{\downarrow}}{Cu}} \leftarrow {:}\overset{H}{\underset{N}{NCH_3}} \right]^{2+} 2Cl^-$$

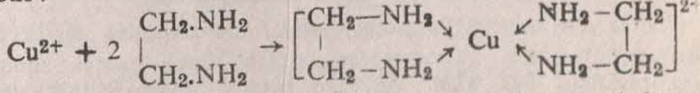
$Co^{3+}$ ion coordinates with six ammonia molecules forming the complex ion $[Co(NH_3)_6]^{3+}$.



$$CO^{3+} + 6 : NH_3 \rightarrow \left[\begin{array}{ccc} H_3N{:}\searrow & & \swarrow{:}NH_3 \\ H_3N{:}\rightarrow & CO & \leftarrow{:}NH_3 \\ H_3N{:}\nearrow & & \nwarrow{:}NH_3 \end{array}\right]^{3+} \text{ or } [CO(NH_3)_6]^{3+}$$

The ammonia molecules in this ion may be replaced one by one by water molecules until an aquecomplex, hexahydrate, is formed, $[Co(H_2O)_6]^{3+}$.

Diamines, such as ethylenediamine, $NH_2.CH_2.CH_2.NH_2$, are bidentate ligands, both the nitrogen atoms bonding to the central metal. For example, ethylenediamine forms a complex with copper (II) ions :



$$Cu^{2+} + 2 \begin{array}{l} CH_2.NH_2 \\ | \\ CH_2.NH_2 \end{array} \rightarrow \left[\begin{array}{l} CH_2-NH_2\searrow \\ | \\ CH_2-NH_2\nearrow \end{array} Cu \begin{array}{l} \swarrow NH_2-CH_2 \\ \qquad\quad | \\ \nwarrow NH_2-CH_2 \end{array}\right]^{2+}$$

In this complex each ethylenediamine molecule is bonded to the copper in two places. Thus the central copper is surrounded by four $-NH_2$ groups, and its coordination number is 4 as in the ammonia complex $[Cu(NH_3)_4]^{2+}$. The ethylenediamine complex has a ring structure (a pair of 5-membered rings). Such a ring structure is called *chelate* pronunced kelate meaning *claw*). Chelated complexes are more stable than similar complexes with unidentate ligands, since their dissociation involves breaking two bonds rather than one.

## 4. Complex ions in Chemical Reactions

1. **Dissociation.** In an aqueous solution, a complex compounds dissociates into a complex ion and the simple ion attached to it. For example,

$$[Cu(NH_3)_4]SO_4 \rightleftharpoons [Cu(NH_3)_4]^{2+} + SO_4^{2-}$$
$$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

However, in solution complex ions dissociate to a certain degree :

$$[Cu(NH_3)_4]^{2+} \rightleftharpoons Cu^{2+} + 4NH_3$$

For this equilibrium,

$$\frac{[Cu^{2+}]\,[NH_3]^4}{[Cu\,(NH_3)_4]^{2+}} = K$$

The greater the constant K, called the *instability constant of the complex ion*, the less stable is the complex For example, from the values of K for the equilibria

$$[Cd(CN)_4]^{2-} \rightleftharpoons Cd^{2+} + 4CN^- \,;\; K = 1{\cdot}4 \times 10^{-17}$$
$$[Cd(NH_3)_4]^{2+} \rightleftharpoons Cd^{2+} + 4NH_3 \,;\; K = 2{\cdot}5 \times 10^{-7}$$

it is evident that the ammonia complex of cadmium is less stable than the cyanide complex.

2. **Exchange Reactions.** In exchange reactions complex ions pass unchanged in composition from one compound to another. For example,

$$2CuSO_4 + K_4[Fe(CN)_6] \rightarrow Cu_2[Fe(CN)_6]\downarrow + 2K_2SO_4$$

Or, ionically,

$$2Cu^{2+} + [Fe(CN)_6]^{4-} \rightarrow Cu_2[Fe(CN)_6]$$

3. **Replacement reactions.** The central metal in complex ions can be replaced by more electropositive metals. For example, silver in the complex $K[Ag(CN)_2]$ is readily replaced by zinc, the latter being more electropositive than silver.

$$Zn + 2K[Ag(CN)_2] \rightarrow 2Ag\downarrow + K_2[Zn(CN)_4]$$

This reaction is used in the extraction of silver from its ores which are first converted into the cyanide complex by treatment with KCN solution, *e.g.*, $AgCl + 2KCN \rightarrow KCl + K[Ag(CN)_2]$.

## 5. Naming the Complex Compounds

In the systematic nomenlature, the complex $K_4[Fe(CN)_6]$ is name potassium hexacyanoferrate (II). Such names sound quite complicated, but when they are broken down to individual parts named according to a few general rules they are really quite simple. Keep in mind that in the formulae of complex compounds, complex anions are associated with positive ions, such as sodium ion, potassium ion, etc., and complex cations are associated with negative ions, such as chloride ion, sulphate ion, hydroxide ion, etc.

In naming complex compounds, *the positive ion is named first followed by the negative ion*, as in all types of compounds. The name of the complex ion is derived according to the following rules.

1. First the ligands are named. The negative ligands all take an -*o* ending, such as $CN^-$ cyano, $Cl^-$ chloro, $NO_2^-$ nitro, etc. Neutral ligands have no special ending. Names of some common neutral ligands are aquo for $H_2O$, ammine for $NH_3$, and nitrosyl for NO.

If the complex contains negative as well as neutral ligands, as in $Na_2[Fe(NO)(CN)_5]$, the negative ligands are named first and then the neutral ligands.

2. If there is more than one of the same ligand present, the number is indicated by using the prefixes di, tri, tetra, penta, hexa, etc.

3. Finally the central atom is named and its valence is shown by a Roman numeral, I, II, III, etc., in parantheses. In the case of complex anions, the central atom takes an *—ate* ending, and the Latin names are used for Fe, Cu, Sn, Pb, and Ag.

4. When writing the name, the complex part is written run on as one word with the oxidation state as part of the word, *i.e.*, with no spacing in between.

These rules are illustrated by the following examples :

A. *Complexes having complex cations.*

| **Formula of the Compound** | **Name of the Compound** |
|---|---|
| 1. $[Cu(NH_3)_4]SO_4$ | Tetramminecopper (II) sulphate |
| 2. $[Co(NH_3)_6]Cl_3$ | Hexamminecobalt (III) chloride |
| 3. $[Ag(NH_3)_2]Cl$ | Diamminesilver (I) chloride |
| 4. $[Ni(H_2O)_6]Cl_2$ | Hexaaquonickel (II) chloride |
| 5. $[Cr(H_2O)_4Cl_2]Cl$ | Dichlorotetraaquochromium (III) chloride. |

B. *Complexes containing complexes anions.*

| **Formula of the Compound** | **Name of the Compound** |
|---|---|
| 1. $K_2[Cu(CN)_3]$ | Potassium tricyanocuprate (I) |
| 2. $K_4[Fe(CN)_6]$ | Potassium hexacyanoferrate (II) |
| 3. $K_3[Fe(CN)_6]$ | Potassium hexacyanoferrate (III) |
| 4. $K_3[Co(NO_2)_6]$ | Potassium hexanitrocobalate (III) |
| 5. $K_2[HgI_4]$ | Potassium tetraiodomercurate (II) |
| 6. $Na_2[Fe(NO)(CN)_5]$ | Sodium pentacyanonitrosyl ferrate(III) |
| 7. $Na_2[SnCl_6]$ | Sodium hexachlorostannate (IV) |

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*Common name is sodium nitroprusside.

## 6. Cyanide Complexes of Iron

**6-1. Potassium ferrocyanide, $K_4[Fe(CN)_6]$.** This compound is named in modern nomenclature as *potassium hexacyanoferrate (II)*. It is formed in solution when an excess of potassium cyanide is added to a solution of an iron salt.

$$Fe^{2+} + 6KCN \rightarrow K_4[Fe(CN)_6 + 2K^+$$

The complex ferrocyanide [more correctly, hexacyanoferrate (II)] ion} is extremely stable and gives none of the common tests for either the ion (II) or the cyanide ions. For the same reason it is not poisonous. In aqueous solutions it dissociates thus

$$K_4[Fe(CN)]_6 \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

Potassium ferrocyanide crystallizes in the form of large, light yellow prisms consisting of the trihydrate, $K_4[Fe(CN)_6].3H_2O$. When it is treated with concentrated sulphuric acid, carbon monoxide is evolved.

$$K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \rightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO \uparrow$$

With iron (III) salts, solution of potassium ferrocyanide give a deep blue precipitate of *Prussian blue*, $KFe[Fe(CN)_6].H_2O$.

$$FeCl_3 + K_4[Fe(CN)_6] \rightarrow KFe[Fe(CN)_6)] + 3KCl$$

With iron (II) salts, a white precipitate $K_2Fe[Fe(CN)_6]$ is formed.

Prussian blue is used as a paint pigment, as laundry bluing, and as a constituent of certain inks.

Potassium ferrocyanide solutions are used as a reagent in the laboratory for the identification of $Fe^{3+}$ ion and for distinguishing between $Fe^{2+}$ and $Fe^{3+}$ ions.

**6-2. Potassium ferricyanide,** $K_3[Fe(CN)_6]$. In modern nomenclature, this compound is known as potassium hexacyanoferrate (III). It is formed by the oxidation of potassium ferrocyanide solution by chlorine, the anion in the former passing from the tetravalent to the trivalent state.

$$2[Fe(CN)_6]^{4-} + Cl_2 \rightarrow [Fe(CN)_6]^{3-} + 2Cl^-$$

$$\text{or, } 2K_4[Fe(CN)_6] + Cl_2 \rightarrow 2K_3[Fe(CN)_6] + 2KCl$$

Potassium ferricyanide crystallizes as dark red crystals which dissolve freely in water giving a yellow solution. In aqueous solutions it dissociates thus :

$$K_3[Fe(CN)_6] \rightleftharpoons 3K^+ + [Fe(CN)_6]^{3-}$$

The addition of an iron (II) salt, $Fe^{2+}$, to potassium ferricyanide solution yields a blue precipitates called *Turnbull's blue*, which has the same composition as Prussian blue, *i.e.*, $KFe[Fe(CN)_6].H_2O$. When solutions of iron(III)ions are added to potassium ferricyanide solution, there is no blue precipitate but only a brown solution.

The reactions of $Fe^{2+}$ and $Fe^{3+}$ ions with potassium ferrocyanide and potassium ferricyanide serve as sensitive tests for distinguishing between $Fe^{2+}$ and $Fe^{3+}$ ions in solution.

## 7. Complex Compounds of Copper

Both cuprous and cupric ions have a strong tendency to form complexes by *coordination of suitable ions or molecules* whereby they attain greater stability.

### 7-1. Cuprous ion complexes

(*i*) *With ammonia.* Cuprous ion, $Cu^+$, co-ordinates with two ammonia molecules to yield *diamminecopper* (*I*) *ion*, $[Cu(NH_3)_2]^+$. Thus cuprous oxide and cuprous chloride dissolve in ammonia solution forming the complex compounds diamminecopper (I) hydroxide, $[Cu(NH_3)_2]OH$, and diamminecopper (I) chloride, $[Cu(NH_3)_2]Cl$, respectively.

$$Cu_2O + H_2O \rightleftarrows 2CuOH \rightleftarrows 2Cu^+ + 2OH^-$$

$$Cu^+ + 2NH_3 + OH^- \rightarrow [Cu(NH_3)_2]OH$$

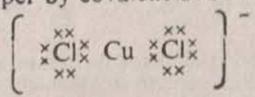
$$CuCl \rightleftarrows Cu^+ + Cl^- ; \qquad Cu^+ + 2NH_3 + Cl^- \rightarrow [Cu(NH_3]_2Cl$$

(*ii*) *With hydrochloric acid.* Cuprous oxide and cuprous chloride dissolve in concentrated hydrochloric acid forming hydrogen dichlorocuprate (I), $H[CuCl_2]$, which contains copper in the anion $[CuCl_2]^-$.

$$Cu_2O + 2HCl \rightleftarrows 2CuCl + H_2O$$

$$CuCl + HCl \rightleftarrows H[CuCl_2] \rightleftarrows H^+ + [CuCl_2]^-$$

This complex compound breaks up on dilution with water to give cuprous chloride. The two chlorine atoms in the $[CuCl_2]^-$ ion are bonded to the copper by covalent bonds.



$$\left[\ \overset{\times\times}{\underset{\times\times}{\overset{\times}{\underset{\times}{}}\text{Cl}\overset{\times}{\underset{\times}{}}}}\ \text{Cu}\ \overset{\times\times}{\underset{\times\times}{\overset{\times}{\underset{\times}{}}\text{Cl}\overset{\times}{\underset{\times}{}}}}\ \right]^-$$

(*iii*) *With cyanide ions.* Cuprous ion, $Cu^+$, co-ordinates with two cyanide ions, $CN^-$, forming the complex dicyanocuprate (I) ion, $[Cu(CN)_2]^-$, *i.e.*, $Cu^+ + 2CN^- \rightarrow [Cu(CN_2)]^-$. This is why alkali cyanide solutions dissolve cuprous salts, *e.g.*, cuprous oxide, etc.

$$Cu_2O + H_2O \rightleftarrows 2CuOH \rightleftarrows 2Cu^+ + 2OH^-$$

$$Cu_2O + H_2O + 4KCN \rightarrow \underset{\text{pot. dicyanocuprate (I)}}{2K[Cu(CN)_2]} + 2KOH$$

The dicyanocuprate (I) ion, $[Cu(CN_2)]^-$ is very stable and this explains why hydrogen cyanide dissolves copper with evolution of hydrogen.

$$HCN \rightleftarrows H^+ + CN^-$$

$$2Cu + 2H^+ \rightarrow 2Cu^+ + H_2\uparrow$$

$$Cu^+ + 2CN^- \rightarrow [Cu(CN)_2]^-$$

## 7.2. Cupric ion complexes

(*i*) *With water*. Cupric salts yield blue tetraaquocopper (II) ion, $[Cu(H_2O)_4]^{2+}$, in aqueous solutions. This is not very stable.

$$Cu^{2+} + 4H_2O \rightleftharpoons [Cu(H_2O)_4]^{2+}$$

(*ii*) *With ammonia*. The cupric ion, $Cu^{2+}$, co-ordinates with four neutral ammonia molecules to yield complex tetrammine-copper (II) ion, $[Cu(NH_3)_4]^{2+}$.

$$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

When ammonia is gradually added to the aqueous solution of a cupric salt, cupric hydroxide, $Cu(OH)_2$, is first precipitated but dissolves in excess of ammonia yielding deep blue solution containing complex tetramminecopper (II) cation.

$$Cu^{2+} + 2NH_4OH \rightarrow Cu(OH)_2\downarrow + 2NH_4^+ \quad ...(1)$$

$$Cu(OH)_{2\,(solid)} \rightleftharpoons Cu(OH)_{2\,(dissolved)} \rightleftharpoons Cu^{2+} + 2OH^- \quad ...(2)$$

$$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} \quad ...(3)$$

The removal of the cupric ions in the ammonia complex shifts the equilibrium in equation (2) to the right until whole of the cupric hydroxide dissolves.

The deep blue solution yields the complex salt containing the tetramminecopper (II) cation and the anion of the original copper salt, *e.g.*, $[Cu(NH_3)_4]SO_4.4H_2O$, $[Cu(NH_3)_4]Cl_2$, etc.

If cupric hydroxide, $Cu(OH)_2$, is separately dissolved in ammonia, the complex compound tetramminecopper (II) hydroxide $[Cu(NH_3)_4](OH)_2$ is produced.

### Questions

1. Define the following terms : (*a*) complex compound, (*b*) ligand and (*c*) coordination number.

2. For each of the following, write the central atom, coordination number of the central atom, the ligands, and the correct name :

(*a*) $[Pt(H_2O)_4]Cl_2$
(*b*) $K_2[ZnCl_4]$
(*c*) $Na_2[PtCl_4]$
(*d*) $[Pt(NH_3)_4]Cl_2$
(*e*) $H[AuCl_4]$
(*f*) $[Co(NH_3)_4Cl_2]Cl$.

3. (*a*) Distinguish between monodentate and bidentate ligands.

(*b*) Write the name and formula of a bidentate.

(*c*) Write the formula of a complex formed by a bidentate ligand.

(*d*) What is the class name given to the complexes formed by bidentates.

4. Write the structural formulae of—

(*a*) ferrocyanide ion.

(*b*) tetramminecopper (II) ion.

(*c*) tetramethylamminecopper (II) ion.

5. Write an explanatory note on the dissociation of complex ions in aqueous solution, giving suitable examples.

6. What types of ions form suitable complexes ?

7. What is the coordination number of copper in the following complexes (*i*) $[Cu(NH_3)_4]^{2+}$ and (*ii*) $[Cu(CH_2NH_2)_2]^{2+}$ ?

Which of the above two complexes is more stable and why ?

8. The addition of a solution of NaOH causes the precipitation of $Ni(OH)_2$ from a solution of $NiSO_4$ but not from a solution of $[Ni(NH_3)_6]SO_4$. Explain the reason.

9. When hydrochloric acid is added in excess to the deep blue solution containing $[Cu(NH_3)_4]^{2+}$, its deep blue colour fades. Explain the reason.

10. What happens when—

(*a*) solutions of copper sulphate and potassium ferrocyanide are mixed,

(*b*) zinc is added to a solution containing the complex $K[Ag(CN)_2]$,

(*c*) ferric chloride is added to a solution of potassium ferrocyanide,

(*d*) ammonia is gradually added in excess to a solution of $CuCl_2$ ?

Give balanced chemical equations.

11. (*a*) How is potassium ferrocyanide formed from a solution containing $Fe^{2+}$ ions ?

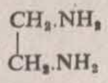
(*b*) What happens when potassium ferrocyanide is heated with concentrated sulphuric acid ?

(*c*) How can potassium ferrocyanide be converted into potassium ferricyanide.

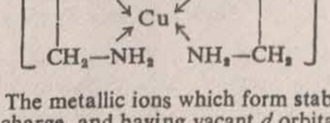
(*d*) What are the systematic names of potassium ferrocyanide and potassium ferricyanide ?

## Key

| 2. | Central atom | Coordination number | Ligand | Correct name |
|---|---|---|---|---|
| (*a*) | Pt | 4 | $H_2O$ | tetraaquoplatinum (II) chloride |
| (*b*) | Zn | 4 | $Cl^-$ | potassium tetrachlorozincate (II) |
| (*c*) | Pt | 4 | $Cl^-$ | sodium tetrachloroplatinate (II) |
| (*d*) | Pt | 4 | $NH_3$ | tetrammineplatinum (II) chloride |
| (*e*) | Au | 4 | $Cl^-$ | hydrogen tetrachloroaurate (III) |
| (*f*) | Co | 6 | $NH_3$, $Cl^-$ | dichlorotetramminecobalt (III) chloride |

3. (*b*) ethylenediamine, 

$$\begin{array}{l} CH_2.NH_2 \\ | \\ CH_2.NH_2 \end{array}$$

(*c*)  (*d*) Chelate.

6. The metallic ions which form stable complex ions are those of small size, high charge, and having vacant *d* orbitals of suitable energy.

7. The coordination number of copper is 4 in both cases as four coordinate bonds are formed in both cases.

The second complex is more stable because its dissociation involves breaking two bonds rather than one.

8. In aqueous solution $NiSO_4$ dissociates as $NiSO_4 \rightleftharpoons Ni^{2+} + SO_4^{2-}$ giving a high concentration of $Ni^{2+}$ so that the product of the concentrations $[Ni^{2+}][OH^-]^2$ exceeds the solubility product $SP_{Ni(OH)_2}$.

The complex $[Ni(NH_3)_6]SO_4$ dissociates in solution as follows:

$$\begin{array}{l} [Ni(NH_3)_6]SO_4 \rightleftharpoons [Ni(NH_3)_6]^{2+} + SO_4^{2-} \\ \qquad\qquad\qquad\quad \Updownarrow \\ \qquad\qquad\qquad\quad Ni^{2+} + 6NH_3 \end{array}$$

The complex ion $[Ni(NH_3)_6]^{2+}$ dissociates to such a small extent that the concentration $[Ni^{2+}]$ is insufficient for the value $SP_{Ni(OH)_2}$ to be reached; so, $Ni(OH)_2$ is not precipitated.

9. In solution $[Cu(NH_3)_4]^{2+}$ dissociates to very small extent:

$$[Cu(NH_3)_4]^{2+} \rightleftharpoons Cu^{2+} + 4NH_3$$

On adding HCl, the ammonia molecules formed by dissociation are used up. To maintain the concentration of ammonia, more of the complex dissociates. This continues until all the complex is completely dissociated. The deep blue colour of the solution due to the $[Cu(NH_3)_4]^{2+}$ changes to light blue colour of the $Cu^{2+}$ ions

11. (*a*) By adding excess of KCN solution.

(*c*) By oxidation with chlorine:

$$2K_4[Fe(CN)_6] + Cl_2 \rightarrow 2K_3[Fe(CN)_6] + 2KCl$$

(*d*) Potassium hexacyanoferrate (II) and potassium hexacyanoferrate (III) respectively.

□ □

# 18

# Nuclear Chemistry

In *chemical changes* only the outer electrons of atoms are involved, the inner parts undergo no change at all. Therefore, the identity of atoms remains unchanged. In *nuclear changes*, the compositions of atomic nuclei are changed as a result of which there is a change into either an atom of a different elelment or a different isotope of the original element. Another very significant feature which distinguishes nuclear changes from chemical changes is that the former are accompanied by rather large energy changes.

The study of nuclear changes, manifested in *radioactivity* (spontaneous, uncontrollable disintegration of atomic nuclei with the emission of penetrating radiations), *atomic transmutations*, and *nuclear fission* and *fusion*, is called **nuclear chemistry**. The knowledge gained in this fascinating field of chemistry has provided valuable information about the structure of all atoms, unlocked the secret to the method of transmuting one element to another, and given mankind a new form of energy, the **nuclear energy**.

## 1. Radioactivity

In 1896, the French scientist Becquerel found that uranium compounds could affect a photographic plate carefully wrapped in thick layers of black paper, and that the intensity of this action was proportional to their uranium content. The obvious conclusion was that the element uranium spontaneously and continuously emitted rays which could penetrate matter opaque to light and darken a photographic plate in the same way that light does when the plate is exposed. Soon afterwards it was found that thorium, an element close to uranium in atomic weight, was also capable of the same action. At Mme Curie's suggestion this property was called *radioactivity* (meaning *ray-emitting activity*), and the substances emitting rays like those emitted by uranium and thorium salts were termed **radioactive**.

Radioactivity may be defined as the property possessed by certain unstable atomic nuclei of undergoing spontaneous, uncontrollable disintegration accompanied with the emission of radiations. The radioactivity of naturally occurring isotopes is called *natural radioactivity*. At present about fifty naturally occurring radioactive isotopes are known, although some of them are only feebly active (like the isotope potassium-40), and others are comparatively rare. All isotopes with an atomic number of 84 or above are radioactive. Radioactivity induced in naturally stable elements by bombarding them with neutrons or other high energy particles is termed *artificial radioactivity* or *induced radioactivity*.

We shall study both kinds of radioactivity in this chapter.

## 2. Nuclear Radiations

There are several types of nuclear radiations given off by radioactive substances; however, the most common are (1) alpha particles, (2) beta particles, (3) gamma rays, (4) positrons*, and (5) neutrons. Of these, only the first three occur in naturally radioactive substances.

The radiations emitted by the nuclei of naturally radioactive substances are of three kinds. These radiations behave differently when passed through two charged plates (Fig. 18-1). One type of radiation is deflected slightly towards the negative plate in the manner of a stream of relatively heavy, positively charged particles. This type of radiation is called alpha rays or *alpha* ($\alpha$) *particles*. Another type of radiation is bent to a much larger extent towards the positive plate in the manner of relatively light particles with a negative charge. This radiation is called beta rays or *beta* ($\beta$) *particles*. The third kind of radiation is not affected by the electric field and continues a straight line. This radiation is called *gamma* ($\gamma$) *rays*.

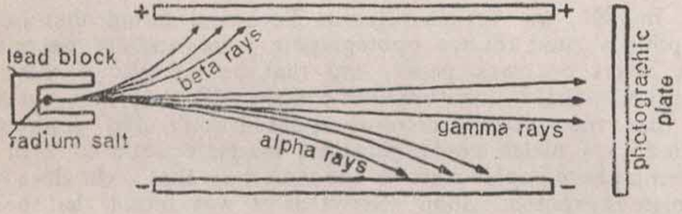


Fig. 18-1. The radiation emitted from a radioactive source placed in a lead block passing through an electric field, with a photographic plate so arranged that a record would be made of the radiations striking it.

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*A positron is found to be a positive electron; that is, it is a particle with negligible mass and a charge of +1. It is represented by the symbol ${}_{+1}^{0}e$. Positrons are believed to be formed in the nucleus of certain radioactive isotopes when a proton is changed to a neutron according to the equation

$$\text{proton, } {}_{1}^{1}p \longrightarrow \text{neutron. } {}_{0}^{1}n + \text{positron, } {}_{+1}^{0}e$$

Positrons have about the same velocity as beta particles, but have very low penetrating power.

**2-1. Alpha particles.** It is experimentally found that alpha particles are the nuclei of helium atoms. Thus the alpha particle is made up of two protons and two neutrons; so it has a charge of +2 and mass of 4. The symbol used for alpha particle is ${}^{4}_{2}He$.

Alpha particles are emitted from atomic nuclei with a rather low velocity, about one-tenth the speed of light. Being relatively heavy, they do not have very high penetrating power. They can pass through about 7-8 cm of air under normal pressure before being stopped. They are stopped by an ordinary piece of paper or by an aluminium foil less than 0·1 mm thick. They have a very powerful *ionizing effect* upon any gas through which they pass. This is because they knock off electrons from the gas molecules with which they collide, changing them into charged particles. At low speeds the alpha particles pick up two electrons each from the atoms with which they collide and become helium atoms. Owing to their high kinetic energy, the alpha particles excite luminescence in zinc sulphide.

**2-2. Beta particles.** The beta particles have been shown to be fast moving electrons. Thus the beta particle has a charge of −1 and a negligible mass. It is represented by the symbol ${}_{-1}^{\ 0}e$.

The beta particles are believed to be produced in the nuclei in the transformation of neutrons into protons in the reaction

$$\text{neutron, } {}^{1}_{0}n \longrightarrow \text{proton, } {}^{1}_{1}p + \text{beta particle } {}_{-1}^{\ 0}e.$$

They are emitted from the nuclei with speeds ranging between 40 and 90 per cent that of light. Because of their minute size and high speed, the beta particles possess about a hundred times greater penetrating power than the alpha particles. They may penetrate a sheet of aluminium about 1 cm thick. Their *ionizing effect* on gases is much less than that of α-particles owing to much smaller kinetic energy (product of mass and velocity). For the same reason, they have little *effect on zinc sulphide*. Their photographic activity is, however, greater than that of the α-particles.

**2-3. Gamma rays.** The gamma rays are electromagnetic radiations similar to X-rays, but of much shorter wavelength. They result from a difference in energy in the original radioactive element and in the more stable product of its disintegration. They do not have any charge or mass, and are represented by the Greek letter γ.

Gamma rays are emitted from the nucleus with a speed nearly equal to that of light. They have very high penetrating power and readily penetrate the human body. They have been detected even passing through 20 cm of lead, 30 cm of concrete, or 60 cm of aluminium. Their ionizing effect is very weak.

The properties of the three kinds of nuclear radiations are summarized in Table 18-1.

**Table 18-1.** *Summary of properties of $\alpha$-, $\beta$- and $\gamma$-rays*

| *Comparison of—* | *$\alpha$-rays* | *$\beta$-rays* | *$\gamma$-rays* |
|---|---|---|---|
| 1. Character | Streams of helium nuclei, mass = 4 ; charge = +2. | Stream of fast moving electrons. charge = —1 ; mass $= \frac{1}{1837}$th of a H atom. | Electromagnetic radiations of short wave-length; electrically neutral and non-material. |
| 2. Deflection in electric field | Curve towards the negatively charged plate. | Curve towards the positively charged plate. | Pass out undeflected. |
| 3. Speed | About 10% that of light. | Between 40 to 90% that of light. | Nearly equal to that of light. |
| 4. Kinetic energy $(m \times v)$ | High | Small | Nil |
| 5. Penetrating power | Low, stopped by Al foil 0·1 mm thick. | About 100 times that of $\alpha$-particles. | About 6,000 times that of $\alpha$-particles. |
| 6. Ionizing effect | High | Low | Very low |
| 7. Effect on ZnS and photographic plate. | Strong | Weak | Weak |

**2-4. Cloud chamber**. The most strikingly convincing proof of the existence of alpha rays is provided by using the apparatus called cloud chamber, devised by the English physicist C.T.R. Wilson. This apparatus makes the tracks of alpha particles visible as a row of droplets which condense from air saturated with water vapour. Its working depends on the fact that water vapour condenses more readily on charged ions than on uncharged molecules.

The principle of a cloud chamber may be explained as follows. If air saturated with water vapour is cooled quickly, droplets of moisture will condense as fog. However, if the air is entirely free of dust the fog will not appear despite the cooling; to form the fog there must be dust particles present around which the vapour can condense. Now ionized gas molecules act as nuclei for the condensation of moisture just as well as do dust particles. If alpha particles are passed through a chamber containing air supersaturated with water vapour, the ions formed along the path of alpha particles will cause minute drops of water to condense around them upon sudden cooling. If the chamber is illuminated laterally, the path of each particle will become visible as a fine trail of fog which can be photographed.

The *Wilson cloud chamber* is shown diagrammatically in Fig. 18-2. It consists of a cylindrical chamber provided with a glass cover at the top and a movable piston at the bottom. When the piston is lowered rapidly, the moist air in the chamber cools due to sudden expansion and becomes supersaturated with water vapour. Fig. 18-3 shows one of the photographs of the fog-tracks of alpha-particles.

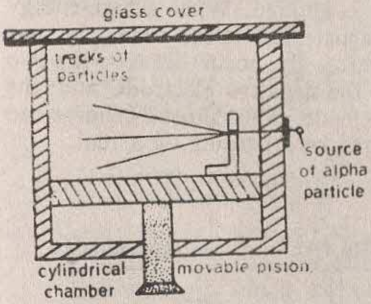

Fig 18-2. The Wilson cloud chamber.

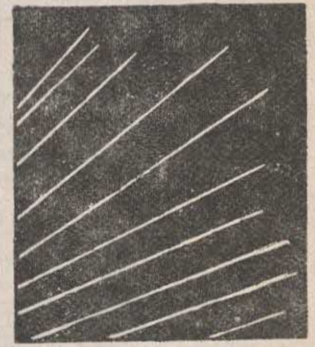

Fig. 18-3. Fog tracks of alpha particles.

The alpha particles travel a maximum distance of 8 cm through the surrounding air before they are stopped completely. Along this path they collide with hundreds of thousands of gas atoms so that their initial velocity is reduced to nothing. However, it is remarkable that despite these collisions the paths of alpha particles, as revealed by the fog tracks are rectilinear. This can be attributed only to the fact that atoms are empty space and the alpha particles fly right *through* them.

A more thorough investigation of this phenomenon led to the discovery of the nucleus of the atom.

**2-5. Physiological effects of nuclear radiations.** Nuclear radiations have disastrous physiological effects, some of them cumulative with time. Exposure to intense radiation causes irreparable damage to living cells; milder radiations can cause anaemia or leukaemia, or can induce malignant (cancerous) growths. Gamma rays affect the genes, causing mutations. Therefore, great care should be taken when working with radioactive substances to avoid exposure to dangerous amounts of radiations.

## 3. Detection and Measurement of Radioactivity

The detection and measurement of radioactivity consists in the detection of the emitted α-, β-, and γ-rays and the measurement of the rate of emission respectively. These radiations are easily detected by their properties of (1) affecting the photographic plate, (2) exciting luminescence in crystalline zinc sulphide, barium platinocyanide (used for γ-rays), etc., and (3) ionizing gases. The rate of emission of the radiations, *i.e.*, the intensity of radioactivity, is measured by making use of their ability to discharge an electroscope. The radiations from radioactive substances ionize air around an electroscope and make it a conductor. This permits the charge on the leaves of the electroscope to leak away. The rate of discharge occurring between the charged leaves is a qualitative measure of the intensity of the radiations from the radioactive substance.

**3-1. Geiger-Muller counter.** This is a well known device for detecting radiation. It consists of a glass tube filled with a gas under low pressure. There are two electrodes sealed inside the tube between which a potential of about 1000V is applied. When a high-energy particle, such as an alpha or a beta particle, enters the tube, the gas inside it is ionized causing conduction to occur between the two electrodes. The positive ions move to the negative electrode and the electrons move to the positive electrode. This short discharge can manifest itself as a click, a flash of light, or a reading on a dial.

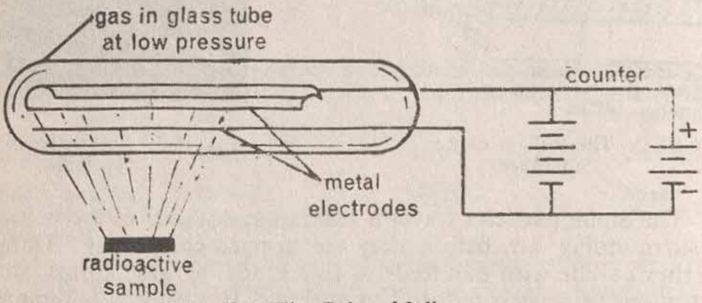

Fig. 18-4. The Geiger-Muller counter.

**3-2. Units of radioactivity.** One of the units used to measure the amount of radioactivity is the *curie* (Ci), named in honour of Madame and Pierre Curie. It is defined as the amount of radiation produced from a radioactive isotope which decays at the rate of $3{\cdot}7 \times 10^{10}$ disintegrations per second. A substance with a radiation of more than 1Ci is considered to have high activity. Frequently, measurement is taken in millicuries; which are equal to one thousandth of a curie.

The unit used to measure the amount of radiation absorbed by biological tissue exposed to radiation is the *roentgen* (*r*), named after Wilhelm Roentgen, the discoverer of X-rays. One roentgen is the amount of gamma radiation that will produce ions carrying 1 electrostatic unit of electricity of either sign in 1cc of dry air.

## 4. Writing Equations for Nuclear Reactions

A process in which a nucleus reacts with another nucleus, or with the elementary particles such as β-particle, neutron, proton, etc., is called a nuclear reaction. The atomic nuclei are represented by the same symbols as their respective atoms, with the mass number and nuclear charge (atomic number) given as superscript and subscript respectively to the left of the symbol. For example, the helium nucleus (an α-particle) is represented as ${}^{4}_{2}He$, 4 being the mass number and 2 the nuclear charge. Similarly, the nucleus of uranium-238 is represented by the symbol ${}^{238}_{92}\mathrm{U}$, 238 being the mass number and 92 the nuclear charge of this isotope. Symbols for some elementary particles are : β-particle ${}^{0}_{-1}e$, neutron ${}^{1}_{0}n$, proton ${}^{1}_{1}\mathrm{H}$, and positron ${}^{0}_{+1}e$.

In writing nuclear equations, the sum of the mass numbers on the left must equal the sum of the mass numbers on the right; likewise, the sum of the charge numbers on the left must equal the sum of the charge numbers on the right, in keeping with the principle of conservation. For example,

$$\begin{array}{lcc} & {}^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \rightarrow & {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H} \\ \text{Mass numbers :} & 14 + 4 = 18 & 17 + 1 = 18 \\ \text{Charge numbers :} & 7 + 2 = 9 & 8 + 1 = 9 \end{array}$$

Similarly,

$$\begin{array}{lcc} & {}^{234}_{90}\mathrm{Th} \rightarrow & {}^{234}_{91}\mathrm{Pa} + {}^{0}_{-1}e \\ \text{Mass numbers :} & 234 & 234+0=234 \\ \text{Charge number :} & 90 & 91+(-1)=90 \end{array}$$

## 5. Changes in Nuclei in Radioactive Emission

The change which occurs in a nucleus during radioactive disintegration depends upon the radiation emitted.

**5-1. α-Particle emission.** An alpha particle, ${}^{4}_{2}\mathrm{He}$, is a combination of two protons and two neutrons so that it has a charge of +2 and mass of 4. When an alpha particle is emitted from a nucleus, the residual nucleus will have nuclear charge (*i.e.*, atomic number) less by 2 units and mass number less by 4 units. [The loss of two protons from the nucleus is accompanied by the loss of two orbital electrons so that the electrical balance in the atom is restored]. The new or *daughter* element, with atomic number less by 2, will have a position two places to the left of the parent element in the periodic table, *i.e.*, two groups to the left. For example,

$$\underset{\text{(in Group II)}}{{}^{226}_{88}\mathrm{Ra}} \xrightarrow{-\alpha} \underset{\text{(in Group 0)}}{{}^{222}_{86}\mathrm{Kn}} + {}^{4}_{2}\mathrm{He}$$

**5-2. β-Particle emission.** The emission of a β-particle, ${}^{0}_{-1}e$, from the nucleus is consequent upon the conversion of a neutron into a proton according to the equation.

$$\underset{\text{(neutron)}}{{}^{1}_{0}n} \rightarrow \underset{\text{(proton)}}{{}^{1}_{1}\mathrm{H}} + \underset{\text{(β-particle)}}{{}^{0}_{-1}e}$$

Since, the neutron and proton have the same mass, the emission of a β-particle does not cause any change in the mass number of the nucleus. However, since the new nucleus has one proton more than the parent nucleus, its nuclear charge or atomic number will be more by one unit. The daughter element will, therefore, have a position one place to the right of the parent element in the periodic table. *i.e.*, in the next higher group. For example,

$$\underset{\text{(in Group IV)}}{{}^{210}_{82}\mathrm{Pb}} \xrightarrow{-\beta} \underset{\text{(in Group V)}}{{}^{210}_{83}\mathrm{Bi}} + \underset{\text{(β-particle)}}{{}^{0}_{-1}e}$$

**5-3. γ-Rays emission**. The emission of γ-rays alone by nucleus does not alter either the atomic number or the mass number since γ-rays possess neither charge nor mass. Their emission results in a nucleus with less energy and, hence, of greater stability. γ-Rays are emitted from nuclei which are left in an excited state by an earlier α-particle or β-particle emission.

**5-4. Group displacement law.*** The results of α- and β-particle changes have been summarized by Fajans and Soddy in the statement called the **group displacement law** :

**Emission of an α-particle gives an element displaced two groups to the left while the emission of a β-particle produces an element that belongs to the next group to the right in the periodic table.**

It follows from the above discussion that a *β-particle change yields an* **isobar** *(same atomic weight, different atomic number) while the emission of an α-particle followed by two β-particle emissions results in the production of an* **isotope** *(same atomic member, different atomic weight)*. For example in the series given below :

$$\begin{array}{lccccccc} & \text{RaA} & \xrightarrow{-\alpha} & \text{RaB} & \xrightarrow{-\beta} & \text{RaC} & \xrightarrow{-\beta} & \text{RaC}' \\ \text{Atomic number} & 84 & & 82 & & 83 & & 84 \\ \text{Mass number} & 218 & & 214 & & 214 & & 214 \end{array}$$

RaB, RaC, and RaC′ are isobaric with one another while RaC′ is isotopic with RaA, being produced from it by one α-particle change and two β-particle changes.

**Problem 1.** *Uranium-238 (atomic number 92) during various disintegration steps loses 8 α- and 6 β-particles. What will be the atomic weight and atomic number of the new product ?*

**Solution**. The loss of an α-particle decreases the atomic weight by 4 units and the atomic number by two units. Hence, the loss of 8 α-particles from $^{238}_{92}\text{U}$ would cause a decrease of 32 units in the atomic weight and of 16 units in the atomic number. Thus, the resulting element will have—

$$\text{Atomic weight} = 238 - 32 = 206$$

$$\text{Atomic number} = 92 - 16 = 76.$$

Emission of a β-particle does not cause a change in the atomic weight but increases the atomic number by 1 unit. Thus, the loss of 6 β-particles will cause an increase in the atomic number by 6 units. Hence, the end product will have

$$\text{Atomic weight} = \mathbf{206}$$

$$\text{Atomic number} = 76 + 6 = \mathbf{82}$$

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*In some cases of artificial radioactivity, the isotopes disintegrate with the emission of positrons, $_{+1}^{0}e$. In such cases, the daughter element is displaced one position to the left since its atomic number will be less by one than that of the parent element.

| Element | Uranium $\xrightarrow{8\alpha}$ | [ ] $\xrightarrow{6\beta}$ | Lead |
|---|---|---|---|
| Atomic number | 92 | 76 | 82 |
| Atomic weight | 238 | 206 | 206 |

**Example 2.** *By natural radioactivity* $^{238}_{92}U$ *undergoes the following changes.*

$$^{238}_{92}\mathrm{U} \rightarrow Ux_1 + \alpha\text{-particle}$$

$$Ux_1 \rightarrow Ux_2 + \beta\text{-particle}$$

*Determine the atomic number and mass number of* $Ux_1$ *and* $Ux_2$.

**Solution**, Loss of an α-particle decreases mass number by 4 units and atomic number by 2 units. Hence,

Atomic number of $\mathrm{U}x_1 = 92 - 2 = 90$

and, mass number of $\mathrm{U}x_1 = 238 - 4 = 234$

That is $$^{238}_{92}\mathrm{U} \xrightarrow{-\alpha} {}^{234}_{90}\mathrm{U}x_1$$

Loss of a β-particle increases the atomic number by 1 unit but does not change the mass number. Hence,

Atomic number of $\mathrm{U}x_2 = 90 + 1 = 91$

and, mass number of $\mathrm{U}x_1$ = that of $\mathrm{U}x_1 = 234$

That is $$^{234}_{90}\mathrm{U}x_1, \xrightarrow{-\beta} {}^{234}_{91}\mathrm{U}x_2$$

It is obvious that $\mathrm{U}x_1$ and $\mathrm{U}x_2$ are isobars.

## 6. Half-life Period

The number of nuclei disintegrating per unit of time for a given radioactive substance is directly proportional to the mass of the substance, *i.e.*, to the total number of atoms of the substance. Therefore, the radioactivity of substance (*i.e.*, the amount of radiation emitted by it) regularly decreases with time, but is never lost completely. The activity of radioactive substances is therefore compared in terms of their half-life periods. *The half-life period* ($t_{1/2}$) *of a radioactive isotope is the time required for one-half of a given mass of the isotope to undergo disintegration* (*and thereby lose half its radioactivity*). This means that whatever be the amount of a radioactive isotope at the start of an investigation, after each half-life period only one-half of its previous amount will remain, the other half will have disintegrated. Thus, the half-life period indicates the activity of a radioactive isotope, since shorter it is, the greater is the number of atoms disintegrating, and vice versa. It also represents the span of time during which the radioactivity of the isotope is useful.

The half-life periods vary enormously with different isotopes. For example, polonium-214 has a half-life of only $1{\cdot}64 \times 10^{-4}$ second while uranium-238 has a half-life of $4{\cdot}51 \times 10^{9}$ years.

Fig. 18-5 shows a typical radioactive disintegration curve. At the end of each half-life period, one-half of the previous amount of the radioactive isotope remains, or, half of its previous activity remains. As this relationship continues indefinitely, no matter how much time passes, a radioactive subsatance will never lose its activity completely. The knowledge of the half-life period concept is very useful in dating past events.

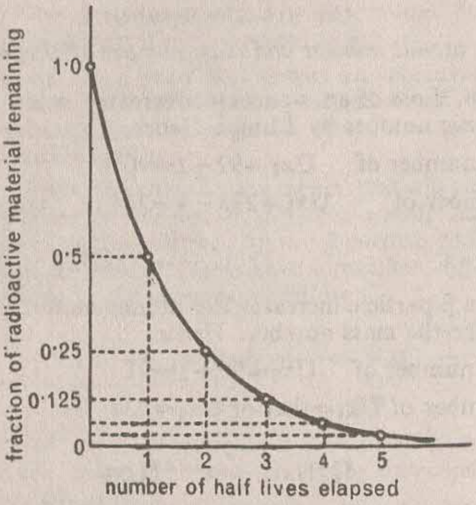

Fig. 18-5. Radioactive disintegration and half-life.

**Problem 18.1.** *The half-life period of radon,* $^{222}_{86}Rn$*, is 4 days. A tube containing 1 microgram (one millionth of a gram, 0·000001 g) of radon was stored for 16 days. How much radon remained in the tube ?*

**Solution.** Every 4 days one-half of the remaining radon will disintegrate. That is,

| *days* | 0 | 4 | 8 | 12 | 16 |
|---|---|---|---|---|---|
| *radon left* | 1·00 | 0·50 | 0·25 | 0·125 | 0·0625 micrograms |

## 7. Radioactive Disintegration Series

A radioactive isotope, being unstable, disintegrates by α- or β-emission to produce a more stable isotope. However, the resulting isotope may still be radioactive and, if so, it too disintegrates. The series of changes occurring in this way stops when a stable, *i.e.*, non-radioactive nuclear species is reached. All the species in one chain, from the initial one to the stable end product, constitute a radioactive disintegration series. A radioactive disintegration series may be defined as a series of isotopes starting with a parent (first member) which changes stepwise into different radioactive isotopes, finally producing a stable (non-radioactive) isotope.

There are three disintegration series of naturally occurring radioactive isotopes These are named the **thorium series**, the **uranium series**, and the **actinium series** after the common radioactive elements thorium, uranium and actinium which belong to these series. Each of the series terminates with an isotope of atomic number 82, lead : the thorium series with $^{208}_{82}$Pb, the uranium series with $^{206}_{82}$Pb, and the actinium series with $^{207}_{82}$ Pb.

The uranium series, originating with $^{238}_{92}$U and ending up with $^{206}_{82}$Pb, is given in Table 18-2. Each step in the series leads to a new isotope until the stable $^{206}_{82}$Pb isotope is formed after a loss of a total of 32 mass units.

**Table 18-2** *The uranium disintegration series*

$$\begin{tikzcd}
{}^{238}_{92}\mathrm{U} \arrow[r, "-\alpha"] & {}^{234}_{90}\mathrm{th} \arrow[r, "-\beta,\gamma"] & {}^{234}_{91}\mathrm{Pa} \arrow[r, "-\beta,\gamma"] & {}^{234}_{92}\mathrm{U} \arrow[r, "-\alpha"] & {}^{230}_{90}\mathrm{Th} \arrow[r, "-\alpha,\gamma"] & {}^{226}_{88}\mathrm{Ra} \arrow[d, "-\alpha,\gamma"] \\
{}^{210}_{82}\mathrm{Pb} \arrow[d, "-\beta,\gamma"] & {}^{214}_{84}\mathrm{Po} \arrow[l, "-\alpha"'] & {}^{214}_{83}\mathrm{Bi} \arrow[l, "-\beta,\gamma"'] & {}^{214}_{82}\mathrm{Pb} \arrow[l, "-\beta,\gamma"'] & {}^{218}_{84}\mathrm{Po} \arrow[l, "-\alpha"'] & {}^{222}_{86}\mathrm{Rn} \arrow[l, "-\alpha"'] \\
{}^{210}_{83}\mathrm{Bi} \arrow[r, "-\beta"] & {}^{210}_{84}\mathrm{Po} \arrow[r, "-\alpha,\gamma"] & {}^{206}_{82}\mathrm{Pb}.
\end{tikzcd}$$

A fourth disintegration series was discovered following the artificial transuranium elements (sec. 11). This series is called the **neptuinium series** after its member of longest half-life. The end product of the series is an isotope of bismuth, $^{209}_{83}$Bi.

The mass numbers of isotopes in any series change only when α-particles are emitted (not when β-particles are emitted). The change in mass numbers, therefore, occurs in units of 4. Thus, the mass numbers of the isotopes in any radioactive disintegration series will all be divisible by 4, or by 4 with a remainder of 1, 2, or 3. Correspondingly, the four disintegration series are referred to as the $4n$ series (thorium series 1), $4n+1$ series (neptunium series), $4n+2$ series (uranium series) and $4n+3$ series (actinium series).

## 8. Transmutation and Decay

In radioactive disintegration, the nucleus of the atom changes to give an atom of a different element or a different isotope of the original element The change of an atom of one element into an atom of another element is commonly referred to as **transmutation**. Transmutations occur naturally in a number of isotopes and can also be effected artificially. When the transmutation is from an element of higher atomic number into one of lower atomic number (as it is in all natural transmutations), the term '**decay**' is often used. In the uranium disintegration series, for example, radium decays to radon and finally, to lead. In fact, the terms radioactive disintegration and radioactive decay are often used interchangeably. Thus, the disintegration series are also called decay series.

## 9. Artificial Transmutation of Elements

It has been found that the nuclear composition of an element can be changed by bombarding it with particles, such as protons, neutrons, electrons, etc., (the element being bombarded is referred to as the *target* element). The resulting nuclear species may produce a new isotope of the same element or an isotope of another element. The first artificial transmutation was caused by Rutherford in 1919. He bombarded nitrogen atoms with alpha particles when the transmutation of nitrogen to oxygen occurred by the following reaction

$$^{14}_{7}\text{N} + ^{4}_{2}\text{He} \rightarrow ^{17}_{8}\text{O} + ^{1}_{1}\text{H}$$

The particle that is to bombard the nucleus in the target element must be accelerated to high speeds, in order to penetrate the nucleus. This is achieved by subjecting the particles to alternate attraction and repulsion in an *accelerator*. Two commonly used accelerators are the *cyclotron* for positively charged particles, and the *betatron* for electrons. Acceleration of positively charged bombarding particles, *e.g*, protons, deuterons (nuclei of deuterium atoms, $^{2}_{1}d$), and alpha particles, also serves to increase their kinetic energy high enough to overcome the repulsion between them and the positively charged nucleus.

Neutrons produced in a nuclear reactor are a favourite bombarding particle because, being uncharged, they are not repelled or attracted by atomic nuclei. Slow neutrons are more effective than fast ones, the high velocity neutrons usually passing through a nucleus without changing it.

We may now define artificial transmutation as *the process of producing new elements by bombarding non-radioactive elements with high velocity particles*. The transmutation reactions are usually classified on the basis of the bombarding particle and the particle ejected in the reaction (the particles are named in this order) as $(n, p)$ reactions, $(p, \alpha)$ reactions, etc. Some of the transmutation reactions are illustrated by the following equations :

$$^{35}_{17}\text{Cl} + ^{1}_{0}n \rightarrow ^{35}_{16}\text{S} + ^{1}_{1}p \qquad (n, p)\ \textit{reaction}$$

$$^{27}_{13}\text{Al} + ^{1}_{0}n \rightarrow ^{24}_{11}\text{Na} + ^{4}_{2}\alpha \qquad (n, \alpha)\ \textit{reaction}$$

$$^{23}_{11}\text{Na} + ^{1}_{1}\text{H} \rightarrow ^{23}_{12}\text{Mg} + ^{1}_{0}n \qquad (p, n)\ \textit{reaction}$$

$$^{12}_{6}\text{C} + ^{1}_{1}\text{H} \rightarrow ^{13}_{7}\text{N} + \gamma \qquad (p, \gamma)\ \textit{reaction}$$

$$^{37}_{17}\text{Cl} + ^{2}_{1}d \rightarrow ^{38}_{18}\text{Ar} + ^{1}_{0}n \qquad (d, n)\ \textit{reaction}$$

The yields in induced nuclear reactions or artificial transmutations are extremely small because only one in about a quarter of a million projectiles is able to hit a nucleus (atom is largely hollow !).

## 10. Artificial Radioactivity

The bombardment of nuclei with high-velocity projectiles often yields isotopes of common elements which are artificially radio-active. They undergo radioactive disintegration into elements of different atomic numbers and have characteristic half-life periods.. *The radioactivity of artificially produced isotopes is called induced, or, artificial radioactivity*. Usually, the man-made radioactive isotopes disintegrate in a single step but the members of neptunium series disintegrate in a series similar to natural disintegration series.

Artificial radioactivity was first discovered by F. Joliot and his wife Irene (daughter of Mme. Curie) in 1934. They bombarded aluminium with alpha particles from polonium when a radioactive isotope of phosphorus was produced with the emission of neutrons.

$${}^{27}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{30}_{15}\mathrm{P} + {}^{1}_{0}n \quad (\alpha, n)\ \textit{reaction}$$

The resulting isotope of phosphorus disintegrates to produce a stable isotope of silicon through a positron emission.

$${}^{30}_{15}\mathrm{P} \rightarrow {}^{30}_{14}\mathrm{Si} + {}^{0}_{+1}e$$

Similarly, the $\alpha$ particle bombardment of boron produces a radioactive isotope of nitrogen, ${}^{13}_{7}\mathrm{N}$ (half-life period 11 minutes), which disintegrates into ${}^{13}_{6}\mathrm{C}$ through a positron emission.

$${}^{10}_{5}\mathrm{B} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{13}_{7}\mathrm{N} + {}^{1}_{0}n \quad (\alpha, n)\ \textit{reaction}$$
$$\llcorner\!\!\longrightarrow {}^{13}_{6}\mathrm{C} + {}^{0}_{+1}e$$

Artificial radioactivity finds application in the production of (1) transuranic elements (*i.e.*, elements with atomic number above 92, (2) elements of atomic numbers 43, 61, 85, and 87, which do not occur in nature, and (3) radioisotopes of various elements.

## 11. Transuranium Elements

Uranium, atomic number 92, is the heaviest naturally occurring element. In 1940, McMillan and Abelson succeeded in creating two new synthetic elements with atomic numbers 93 and 94 which were named neptunium (Np) and plutonium (Pu) respectively. They bombarded natural uranium, ${}^{238}_{92}\mathrm{U}$, with neutrons when a heavier isotope, ${}^{239}_{92}\mathrm{U}$, was produced. This isotope yielded neptunium and plutonium by two successive beta emissions.

$${}^{238}_{92}\mathrm{U} + {}^{1}_{0}n \rightarrow {}^{239}_{92}\mathrm{U} \xrightarrow{-\beta} {}^{239}_{93}\mathrm{Np} \xrightarrow{-\beta} {}^{239}_{94}\mathrm{Pu}$$

Plutonium is now being made on a large scale for the production of atomic energy and atomic missiles.

Besides these two man-made or synthetic elements, nuclear scientists have created by similar processes eleven more elements with atomic numbers rising continuously up to 105. These are *americium* (95), *curium* (96), *berkelium* (97), *californium* (98), *einsteinium* (99), *fermium* (100), *mendelevium* (101), *nobelium* (102), *lawrencium* (103), *rutherfordium* (104), *and halihium* (105). All transuranic elements are radioactive and most of them have short half-lives.

## 12. Radioactivity and Chemical Change

Radioactive disintegration results in the formation of new substances, like it is with chemical changes. Radioactivity is, however, distinct from chemical change in the following respects :

1. Radioactivity is not influenced by physical conditions such as temperature and pressure, or by the effects of electric or magnetic fields.

2. The radioactivity of an element remains unaffected by other element or elements compounded with it. One milligram of say radium, whether in the elementary state or in any one of its salts, *e.g.*, radium bromide, radium, nitrate, etc., produces the same intensity of radioactivity. This shows that *radioactivity is a nuclear property and does not involve outer electron activity.*

3. Radioactivity is associated invariably with the liberation of vast amounts of energy—about $10^7$ to $10^8$ times as much as that liberated in a chemical change involving the same weight of a substance.

4. Radioactivity involves the nucleus of the atom which undergoes a thorough change; ordinary chemical changes involve only the rearrangement of outer electrons, while the atomic nuclei remain unaffected.

## 13. Nuclear Fission

When certain heavy atoms, *e.g.*, uranium-235 or plutonium-239 are bombarded with neutrons, they split into two nearly equal parts. The change is accompanied with the release of two or more new high-velocity neutrons per nucleus split up and a large amount of energy. *This process of a heavy nucleus splitting into more stable nuclei with mass numbers from 83 to 154 is known as* **nuclear fission.** *The products of nuclear fission, which are intensely radioactive, are called fission products.*

In the case of $^{235}U$, the following equation represents one mode of nuclear fission, out of many possible :

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}n \rightarrow {}^{140}_{56}\mathrm{Ba} + {}^{93}_{36}\mathrm{Kr} + 3\,{}^{1}_{0}n$$

The total mass of fission products is about 0·2 mass units less than the mass of the uranium atom and a neutron. This corresponds to the release of a large amount of energy since energy and mass are related by the equation $E = mc^2$, where $E$ is energy in ergs, $m$ is mass in grams, and $c$ the velocity of light in cm/sec.

The energy released in nuclear fission is called the *nuclear energy* or the *atomic energy.* The energy liberated from the nuclear fission of a kilogrom of uranium-235 is about 2·5 million times as much as that produced by burning of a kilogram of coal.

The neutrons released during nuclear fission may cause the fission of other nuclei when more neutrons are emitted. Thus a **chain reaction** is set up which will maintain itself indefinitely. The chain reaction can be kept under control by using substances which absorb neutrons. In an **atomic bomb** the chain reaction is allowed to build itself up at maximum speed so that all the atoms of U-235 or Pu-239 undergo fission simultaneously liberating terrific amounts of energy.

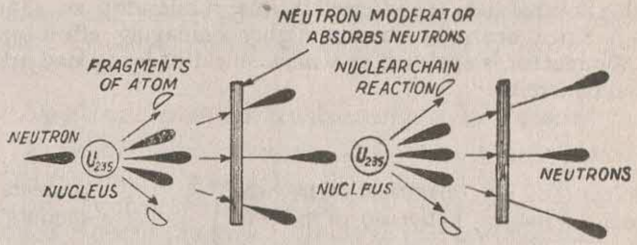

Fig. 18-6. Chain reaction in the fission of U-235.

## 14. Nuclear Fusion

The fusion of two light nuclei into a heavier and more stable nucleus is also accompanied by large conversions of mass into energy. Such reactions are called **nuclear fusions**. Thus, at a temperature of about 10,000,000°C produced by exploding a fission type bomb, deuterium, $^{2}_{1}H$, and tritium, $^{3}_{1}H$, fuse to form helium and a neutron.

$$^{2}_{1}H + ^{3}_{1}H \rightarrow ^{4}_{2}He + ^{1}_{0}n + energy$$

This change is accompanied by a conversion of about 0·4 per cent of mass into energy. This nuclear reaction forms the basis of the hydrogen bomb. Hydrogen bomb can be made thousands of times more destructive than the fission type atomic bomb because more energy is liberated per gram fuel (reactants) in a fusion reaction than in a fission reaction.

## 15. Nuclear Reactors

A nuclear reactor is a device to keep the chain reactions of fissionable materials under control so that they can deliver a constant supply of heat energy and serve as a convenient source of neutrons for producing plutonium, etc. It consists of three components :

(1) The **fissionable material** or **fuel** such as uranium, plutonium, etc., sealed in aluminium cans. It is also called the **core** of the reactor.

(2) A **moderator** such as highly purified graphite, and pure heavy water, to reduce the velocity of neutrons. When graphite

is used as the moderator, the reactor is usually called an **atomic pile**; when heavy water is used, it is called a **swimming pool reactor**.

(3) **Control rods** of cadmium or boron steel to absorb neutrons. Whenever the chain reaction becomes violent, these rods are pushed into the pile.

The aluminium cans containing the fissionable material and removable control rods are inserted in the moderator as shown in Fig. 18-7. Since neutrons have a highly damaging effect on living tissues, the reactor is enclosed in a thick shield of lead, lead glass, or of special concrete.

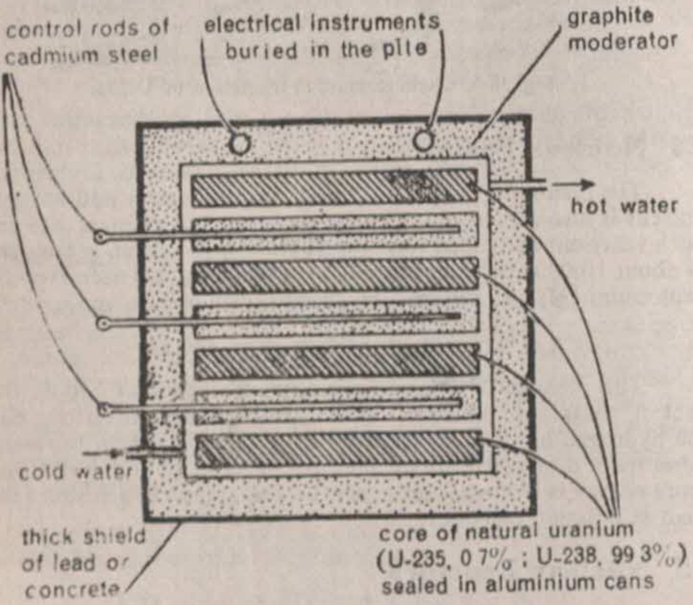
control rods of cadmium steel
electrical instruments buried in the pile
graphite moderator
hot water
cold water
thick shield of lead or concrete
core of natural uranium (U-235, 0.7% ; U-238, 99.3%) sealed in aluminium cans

Fig. 18-7. An atomic pile.

The reaction is started by stray neutrons from cosmic rays. The neutrons released during the fission keep the chain reaction going. The thermal energy produced as a result of nuclear fission is constantly removed by using a **coolant**. Air, carbon-dioxide, water, liquid sodium, etc., have all been used for this purpose. For producing plutonium, a valuable fissile material, 'core' of uranium is used in the reactor. Most of the neutrons' not used in causing further fission cause uranium-238 to change into plutonium by the following reactions :

$$\begin{aligned} {}^{238}_{92}U + {}^{1}_{0}n \rightarrow {}^{239}_{92}U \xrightarrow{23\text{ min.}} {}^{239}_{93}Np + {}^{0}_{-1}e \\ \xrightarrow{2\cdot3\text{ days}} {}^{239}_{94}Pu + {}^{0}_{-1}e \end{aligned}$$

Often, other elements enclosed in aluminium cans are temporarily inserted into the pile. Here they are subjected to intense radiation and converted into radioactive isotopes. Many of the radioactive isotopes thus produced find a wide variety of applications in different fields.

## 16. Applications of Radioactive Isotopes*

**1. In medicine.** Radioactive isotopes which produce strong gamma radiations are used for the radiation treatment of cancer. Radioactive cobalt, $^{60}Co$ (half-life 5·25 years), has largely replaced the more expensive radium. It is called the 'the poor man's radium'. Iodine-131 (half-life 8 days) is used internally in the treatment of the cancer of the thyroid gland because of its tendency to accumulate thereafter ingestion. Radioactive phosphorus is used for internal irradiation of bone marrow.

**2. For dating inorganic and organic material.** Radioactive isotopes are extremely useful in dating past events. The age of certain rocks and mineral deposits has been estimated by measuring the ratio of uranium to lead. These estimations give an age of around 4·5 billion ($4{\cdot}5 \times 10^9$) years for the earth's crust.

*Radiocarbon dating.* By using the half-life of the radioactive isotope $^{14}C$, it is possible to estimate the age of archeological objects consisting of organic material, *e.g.*, wooden objects. The cosmic rays bombarding the atmosphere produce neutrons which cause a very small proportion of nitrogen atoms to transform into $^{14}C$.

$${}^{14}_{7}N + {}^{1}_{0}n \rightarrow {}^{14}_{6}C + {}^{1}_{1}H$$

The numer of cosmic rays entering the atmosphere from outer space being relatively constant, there has been an equilibrium between the $^{14}C$ and $^{12}C$ content of atmospheric carbon dioxide for ages. The atmospheric carbon dioxide is incorporated into vegetation by photosynthesis and, in turn, into animals feeding on vegetation. Thus, the ratio of $^{14}C$ to $^{12}C$ (which is not radioactive) remains fairly constant in all living organisms, plants or animals. When the living organism dies, it no longer takes in $CO_2$ from the atmosphere, and the amount of $^{14}C$ in the remains decreases through radioactive decay. The half-life of carbon-14, a beta emitter, is 5570 years. So, after 5570 years one-half of carbon-14 remains. After 2×5570 years $\frac{1}{2}\times\frac{1}{2}$, *i.e.*, one-fourth of carbon-14 remains. After 3×5570 years $\frac{1}{2}\times\frac{1}{2}\times\frac{1}{2}$, *i.e.*, one-eighth of carbon-14 remains, and so on. So, if an

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*Radioactive isotopes are often called *radioisotopes*.

old piece of wood has only half the beta-ray emission per gram of carbon of a new, growing piece of wood, its age is 5570 years.

This method of dating organic material is called radiocarbon dating.

3. **In industry**. Radioactive isotopes are use to locate cracks and flaws in castings. The rays pass through the castings and are photographed. The 'radiographs' thus obtained reveal any defects. Foods, drugs, etc., are often sterilized by exposure to radioactive rays at normal temperatures. Radioactive isotopes are used for determining the thickness of thin foils, paper, etc. by measuring the attenuation of their radiation on passing through the material. Other uses are checking the wear of material surfaces, determining leaks in flow lines, for ionizing air to eliminate accumulation of static electricity during industrial processes where there is a risk of fire, etc.

4. **As tracers or radioactive indicators.** A radioactive isotope continually gives out radiation which can be easily detected by means of, say, a Geiger counter. This permits its course to be followed through a series of chemical or physical changes. In practice use is often made of compounds containing a radioisotope of one of the elements, *e.g.*, $^{24}_{11}Na$ in sodium chloride and $^{32}_{15}P$ in phosphates. Such compounds are known as '*tagged*' or '*labelled*' compounds. Employed in this way radioisotopes are used to study the mechanisms and kinetics of chemical reactions, to investigate metabolic processes, and for other similar studies. For example, radioactive iron is used to study the mechanism of iron absorption in red blood cells, radioactive calcium to study bone and tooth formation, and radioactive phosphorus and potassium to study formation of nerve tissue. Since a growing tumour preferentially absorbs iodine, injected radioactive iodine compounds are used to locate a brain tumour. The conversion of $CO_2$ by plants into various compounds and eventually into carbohydrates has been investigated by using tagged molecules containing C-14.

5. **In the determination of solubilities of sparingly soluble salts**. The solubility of $PbSO_4$ in water, for example, is estimated by mixing a known amount of radioactive lead (Pb*) with ordinary lead and dissolving the mixture in nitric acid. The solution is treated with $H_2SO_4$ when $PbSO_4$ is precipitated.

$$Pb^* + Pb \xrightarrow{HNO_3} Pb^*(NO_3)_2 + Pb(NO_3)_2 \xrightarrow{H_2SO_4} Pb^*SO_4\downarrow + PbSO_4\downarrow$$

The precipitated lead sulphate is filtered off. The amount of lead sulphate present in the filtrate in the dissolved state is determined by measuring the activity of radio lead (Pb*).

## Questions

1. (*a*) Define radioactivity.

(*b*) What is the essential difference between a radio-active and a nonradioactive isotope.

2. (*a*) What are alpha, beta, and gamma rays ?

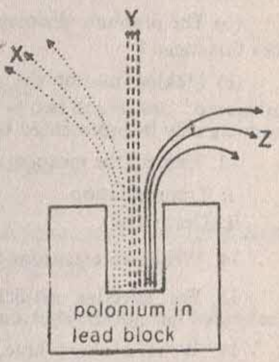
(*b*) Why do $\beta$-particles have greater penetrating power than the $\alpha$-particles emnating from a radioactive substance ?

(*c*) When passed through an electric field, the $\alpha$-particles are deflected very slightly towards the negative plate, the $\beta$-particles are deflected to a far greater extent in the opposite direction, while $\gamma$-rays pass out undeflected. Explain these observations.

3. The figure given in the margin represents nuclear radiations in a magnetic field perpendicular to the plane of paper.

(*i*) Identify *x*, *y* and *z*.

(*ii*) Compare the penetrating power and the ionizing effect of each kind of rays—*x*, *y*, and *z*.



4. Explain the use of the Wilson cloud chamber in the detection of $\alpha$-rays.

5. Why is it necessary to take great care when working with radioactive substances ?

6. (*a*) Describe the construction and working of Geiger-Muller counter.

(*b*) Define the two common units used to measure the amount of radioactivity.

7. Rutherford in 1919 found that an isotope of oxygen, $^{17}_{8}O$ could be produced by bombarding $^{14}_{7}N$ with alpha particles. The reaction can be written as

$$^{14}_{7}N + ^{4}_{2}He \rightarrow ^{17}_{8}O + ^{1}_{1}H$$

(*a*) What do you understand by $^{1}_{1}H$ ?

(*b*) Is this an example of induced radioactivity or of artificial transmutation ?

(*c*) Is this an example of nuclear fission ? Give your own example of nuclear fission ?

(*d*) What is an atomic reactor ?

(*e*) What are radio-isotopes ? State *one* use of such isotopes.

8. Complete the following nuclear equations :

(*a*) $^{60}_{27}Co \rightarrow \ldots + \beta$

(*b*) $^{16}_{8}O + ^{1}_{0}n \rightarrow \ldots + ^{4}_{2}\alpha$

(*c*) $^{40}_{20}Ca + \ldots \rightarrow ^{41}_{21}Sc$

(*d*) $^{37}_{18}Ar + — \rightarrow ^{37}_{17}Cl$

(*e*) $^{23}_{11}Na + ^{2}_{1}H \rightarrow ^{21}_{10}Ne + \ldots$

(*f*) $^{9}_{4}Be + ^{4}_{2}He \rightarrow \ldots + ^{1}_{0}n.$

9. Write equations for the following processes :

(*a*) $^{14}_{7}\text{N}\ (n, p)$, (*b*) $^{15}_{7}\text{N}\ (p, \alpha)$, (*c*) $^{16}_{8}\text{O}\ (n, \alpha)$ (*d*) $^{27}_{13}\text{Al}\ (\alpha, p)$.

10. (*a*) How does the composition of a nucleus change when it loses an α-particle ? A beta particle ?

(*b*) State the group displacement law.

11. (*a*) Write a short note (6-7 lines) on the half-life period of a radioactive substance.

(*b*) What is meant by saying that the half-life of a radioactive isotope is 24 days ?

12. (*a*) There are four different radioactive disintegration series. One of these differs from the other three in the end element. Name this series.

(*b*) The uranium disintegration series is referred to as $(4n+2)$ series. What does this mean ?

(*c*) Making use of the radioactive element $^{238}_{92}\text{U}$, show that by successive emission of one α- and two β- particles an isotope is obtained. (The successive products may be represented by the symbols X, Y and Z).

13. Explain the meaning of each of the following terms :

*i*. Transmutation
*ii*. Decay
*iii*. Nuclear fission
*iv*. Nuclear fusion.

14. Write two equations to illustrate artificial transmutation of elements.

15. For effecting artificial transmutations, the α-particles and protons are acclerated but not the neutrons. Why ?

16. Write a short note, with a suitable example, on either 'artificial radioactivity' or 'transuranic elements'.

17. In what respects is radioactivity different from chemical changes ?

18. Give a brief account of nuclear fission and the energy released as a result thereof.

19. Write an explanatory note on nuclear fusion.

20. Describe the main parts of a nuclear reactor and its working.

21. (*a*) Give a brief account of the typical uses of radio-isotopes.

(*b*) A radioactive isotopes of a certain element called 'the Poor Man's Radium' is used for the treatment of cancer. Name the element of the isotope.

22. Describe in brief the method of radiocarbon dating.

23. State with reasons whether each of the following statements is true or false ?

(*a*) Isotopic atoms have the same mass numbers.

(*b*) Emission of an alpha particle results in the loss of two positive charges from the nucleus of the radioactive atom.

(*c*) Loss of an electron from the nucleus of an atom puts it in the next higher group of the periodic table.

(*d*) Gain of a neutron is equivalent to the gain of an atomic number.

(*e*) Beta rays are streams of negatively charged particles.

(*f*) Nuclear fission usually results in the release of a large amount of energy.

## Key

1. (*b*) The nuclei of radioactive isotopes are unstable, spontaneously undergoing disintegration by the loss of α-particles or β-particles to change into more stable nuclei. With nonradioactive isotopes no such process occurs.

2. (*b*) Because of their minute size and high speed.

(*c*) Owing to their positive charge, the α-particles are deflected towards the negative plate while the β-particles, owing to their negative charge, are deflected in the opposite direction, *i.e.*, towards the positive plate. The smaller deflection of α-particles is due to their heavy mass and large momentum. The heavy deflection of β-particles is due to their mass and momentum being much smaller. The γ-rays are not deflected as they have no charge.

3. *i*) X : α-particles (large deflection)

Y : γ-rays (no deflection)

Z : β-particles (large deflection)

(*ii*) Pentrating power : γ-rays>β-rays>α-rays

Ionizing effect : α-rays>β-rays>γ-rays.

7. (*a*) $^{1}_{1}\mathrm{H}$ stands for a proton or hydrogen nucleus.

(*b*) Artificial transmutation.

(*c*) It is not an example of nuclear fission. An example of nuclear fission is

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}n \rightarrow {}^{140}_{56}\mathrm{Ba} + {}^{93}_{36}\mathrm{Kr} + 3\,{}^{1}_{0}n$$

8. (*a*) $^{60}_{28}\mathrm{Ni}$ (*b*) $^{13}_{6}\mathrm{C}$ (*c*) $^{1}_{1}\mathrm{H}$ (*d*) $^{0}_{-1}e$ (*e*) $^{4}_{2}\mathrm{He}$ (*f*) $^{12}_{6}\mathrm{C}$.

9. (*a*) $^{14}_{7}\mathrm{N} + {}^{1}_{0}n \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}p$

(*b*) $^{15}_{7}\mathrm{N} + {}^{1}_{1}p \rightarrow {}^{12}_{6}\mathrm{C} + {}^{4}_{2}\alpha$

(*c*) $^{16}_{8}\mathrm{O} + {}^{1}_{0}n \rightarrow {}^{13}_{6}\mathrm{C} + {}^{4}_{2}\alpha$

(*d*) $^{27}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{30}_{14}\mathrm{P} + {}^{1}_{1}\mathrm{H}$

11. (*b*) The statement means that any given amount of the radioactive isotope will be reduced to exactly one-half at the expiry of 24 days, and its activity (amount of radiation emitted) will correspondingly be reduced to one-half.

12. (*a*) Neptunium series.

(*b*) The mass numbers of all isotopes constituting the series are devisible by four with remainder of 2.

(*c*) $^{238}_{92}\mathrm{U} \xrightarrow{-\alpha} {}^{234}_{90}\mathrm{X} \xrightarrow{-\beta} {}^{234}_{91}\mathrm{Y} \xrightarrow{-\beta} {}^{234}_{92}\mathrm{Z}$.

23. (*a*) False. Isotopic elements have the same number of protons but different number of neutrons in their nuclei; so, their mass numbers (sum of protons and neutrons) are different.

(*b*) True. Alpha particles carry a charge of +2; so, the emission of an alpha particle from the nucleus will cause the positive charge on it to be reduced by 2 units.

(*c*) True. Loss of an electron involves the conversion of a neutron in the nucleus into one proton; as such, the nuclear charge, or, the atomic number is increased by one.

(*d*) False. The atomic number is determined by the number of protons in the nucleus and not by the number of neutrons.

(*e*) True. The beta rays are deflected in an electric field towards the positive plate.

(*f*) True. Nuclear fission is accompanied by some loss in mass which is converted into energy according to the equation $E=mc^2$.

## Problems

1. The following data was obtained from a Geiger Counter in respect of a radioactive isotope :

| *Time (min)* | *Counts/min* |
|---|---|
| 0 | 1000 |
| 5 | 800 |
| 10 | 650 |
| 15 | 500 |
| 20 | 350 |

(*a*) Calculate the half-life of the isotope.

(*b*) What will be the number of counts/min at the 30th minute ?

[**Ans.** (*a*) 15 minutes, (*b*) 250]

2. If the half-life period of a radioactive element is 4 years and the initial amount is 0·16 g, how much of it will be left over after 12 years ? [**Ans.** 0·02 g]

3. A radioisotope has a 5-year half-life. After a given amount decays for 15 years, what fraction of the original isotope remains ? [**Ans.** 1/8]

4. (*a*) If an atom of radium, $^{228}_{88}\text{Ra}$, decays by the loss of a β-particle, what is the relative atomic mass, and the atomic number of actinium (symbol Ac) atom formed. Give the symbolic representation also.

(*b*) Again, if the resulting atom of actinium, Ac, undergoes further decay by the loss of one alpha particle, what will be the relative atomic mass and atomic number of the resulting atom of radon (symbol Rn).

[**Ans.** (*a*) $^{228}_{89}\text{Ac}$ (*b*) $^{224}_{87}\text{Rn}$]

5. Neutrons produced by the interaction of cosmic rays and atomic nuclei enter into the following reaction with atmospheric nitrogen :

$$^{14}_{7}\text{N} + ^{1}_{0}n \rightarrow ^{14}_{6}\text{C} + \text{X}$$

Give the name, atomic number, and mass number of X. [**Ans.** Proton, 1, 1]

6. The atom of an elements X with atomic number 15 and mass number 31 absorbs one neutron when irradiated with neutrons and is converted to its radioactive isotope Y which is a beta emitter. Isotope Y then decays and is changed to an element Z which forms a gaseous hydride of formula $H_2Z$.

(*a*) Deduce the mass number and atomic number of Z.

(*b*) What is the molecular weight of $H_2Z$ ?

(*c*) To which groups of the periodic table do X, Y, and Z belong ?

(*d*) What are the molecular formula and molecular weight of the hydride of Y ?

[**Ans.** (*a*) Mass no. 32; At. No. 16.

(*b*) 34 $(2\times1+32)$.

(*c*) The atomic numbers of X, Y and Z being 15, 15 and 16, they belong to Groups V, V and VI respectively.

*d*) $YH_3$ (∵ Belonging to group V, the valency of Y is 3).]

7. When a radioactive element of atomic weight 230 gave out $6 \times 10^{12}$ disintegrations it decreased in mass by $2{\cdot}3 \times 10^{-6}$ mg. How many disintegrations will be produced when it loses one gram atomic weight of the element ?

[**Ans.** $6 \times 10^{20}$]

[**Hint.** $2{\cdot}3 \times 10^{-6}$ mg : $6 \times 10^{12}$ disintegrations = 230 g : *n* disintegrations].

8. A radioactive element A emits α-particles and is converted into another radioactive element B which is a beta emitter. B is changed to C which is another beta emitter. The final product formed is D.

(*a*) If the mass number of A is 238 and its atomic number is 92, deduce the mass numbers and atomic numbers of B, C and D.

(*b*) If A belongs to group VI of the periodic table, indicate the groups to which B, C and D belong.

[**Ans.** (*a*) Mass numbers : B=234; C=234, D=234;
Atomic numbers : B=90, C=91, D=92.

(*b*) B, Group IV; C, Group V; D, Group VI.

□ □

# PART III

# Organic Chemistry

# 19

# Some Basic Concepts

In general, organic compounds exist as covalent molecules—a fact which accounts for their general characteristics such as low melting points, low boiling points, poor solubility in water and high solubility in nonpolar solvents, lack of electrical conduction in water solutions, etc. In the covalent bond there is a sharing of one, two, or three valence pair of electrons between the associated atoms. However, this simple treatment of covalent bond formation is inadequate for understanding the nature of chemical bonding in organic compounds, and calls for further elaboration.

In this chapter we shall study the concepts of orbital overlap in covalent bond formation, sigma and pi bonds, and the hybridization of atomic orbitals, which are of great value in understanding, describing, and predicting the geometry of organic molecules.

## 1. Orbital Overlap in Covalent Bonding

The covalent bond is formed by the coalaescing or overlapping of atomic orbitals. This may be illustrated with the formation of the hydrogen molecule, $H_2$, from two separate hydrogen atoms.

$$H_{(g)} + H_{(g)} \rightarrow H_{2(g)} + 435 \text{ kJ}$$

The equation shows that the formation of 1 mole of $H_2$ molecules is accompanied with the release of 435 kJ of energy. Obviously, the $H_2$ molecule has lower energy and is, therefore, more stable than two separate hydrogen atoms.

A free hydrogen atom consists of a proton (the positively charged nucleus) surrounded by a spherical electron cloud corresponding to the 1*s* electron. When two hydrogen atoms with opposite spins approach each other, their nuclei exert a force of repulsion and so do their electron clouds. However, as the atoms approach closer, the forces of attraction between the nucleus of one and the electron cloud of the other emerge (Fig. 19-1), and the energy of the system is decreased. The energy falls and reaches a minimum value at a certain internuclear distance, any closer approach causing a sharp rise in internuclear repulsion (Fig. 19-2, curve 1). The minimum on the energy curve indicates the gain in energy, E, during the formation of $H_2$ molecule from free H atoms and corresponds to the most stable internuclear distance, $r_o$, in the $H_2$ molecule. This distance is the equilibrium *bond length* in the molecule. In the hydrogen atoms with parallel spins, only the forces of repulsion exist and the forces of attraction do not arise (Fig. 19-2, curve 2).

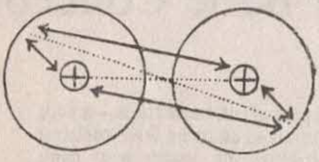


Fig. 19-1. Forces acting between two hydrogen atoms; the electron clouds are shown by large circles, the forces of attraction by ←→, and the forces of repulsion by....

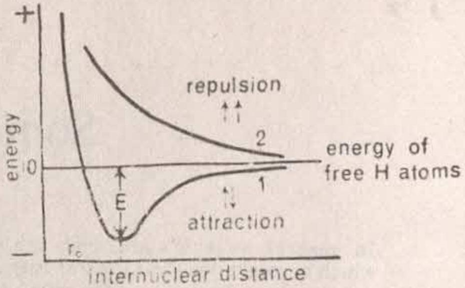


Fig. 19-2. Variation in the potential energy of a system of two hydrogen atoms with internuclear distance; curve 1 for atoms with opposed electron spins, curve 2 for atoms with parallel electron spins.

The formation of the $H_2$ molecule at the internuclear distance corresponding to minimum energy results from the partial overlapping of the 1*s* orbitals of the two hydrogen atoms. This is represented in Fig. 19-3.

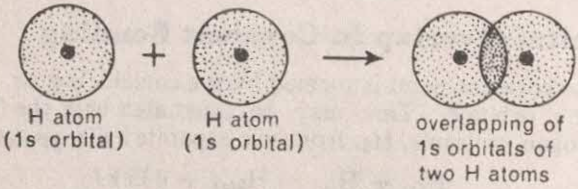


Fig. 19-3. Overlapping of the 1*s* orbitals of two hydrogen atoms in the formation of $H_2$ molecule (shading represents the electron clouds; inner black circles represent nuclei). Note that the electron density is maximum in the region in which the orbitals overlap.

As a result of orbital overlap, each of the two electrons comes in the field of both atomic nuclei. Since each electron is electrostatically attracted by two nuclei rather than by one (as in the separated atoms), the new system is more stable than two isolated hydrogen atoms. It is the simultaneous attraction of the two nuclei for the electrons that holds the atoms together and constitutes a chemical bond between them. The bond arising from the overlapping of orbitals is called a *covalent bond*. It is usually shown by a dash placed between the atoms linked together, *e.g.*, H – H, which signifies a pair of electrons shared between the atoms each of which has contributed one electron to the shared pair. The sharing of electrons is often shown by representing valence electrons as dots placed between the atoms :

$$H^{\cdot} + .H \rightarrow H:H$$

**1-1. Conditions for orbital overlap**. When two atoms whose electrons have parallel spins approach each other, the energy increases and repulsive forces alone are manifested (curve 2, Fig. 19-2). Hence, their orbitals do not overlap and no bonding takes place. Thus, two conditions essential for orbital overlap and the formation of a covalent bond are :

1. Each of the two orbitals which will overlap must have a single electron, and their electrons must have opposed spins.

2. The two atoms must be situated at a distance at which the system will have the lowest energy.

These conditions apply to covalent bond formation in all molecules. It must also be remembered that only valence electrons are used to form the bond; inner electrons being too strongly bound to their own atom to be used in bond formation.

## 2. Molecular Orbital

The overlapping of two atomic orbitals, each containing an unpaired electron of opposed spin, results in the formation of a new single orbital. The new orbital is called a *molecular orbital*, and it surrounds both of the nuclei in the molecule. The Pauli exclusion principle also applies to molecular orbital, and it cannot contain more than two electrons of opposed spins. It follows, therefore, that each of the atomic orbitals involved in the formation of a covalent bond must contain but a single electron.

Although each of the 'paired' electrons may be found anywhere within the molecular orbital, they are more likely to be in the region between the two nuclei because of their being attracted by both the nuclei. This is represented by a pulling in of the electron cloud from the far side of each atom to the centre of the molecular orbital (Fig. 19-4). Note in this figure, that the density of electron cloud is greater in the region between the nuclei than at the ends of the molecule.

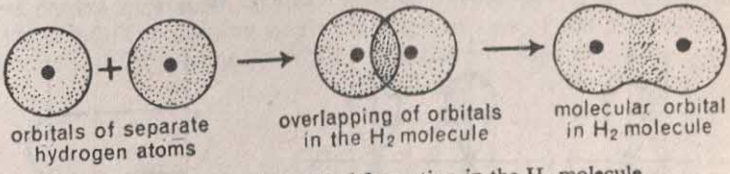
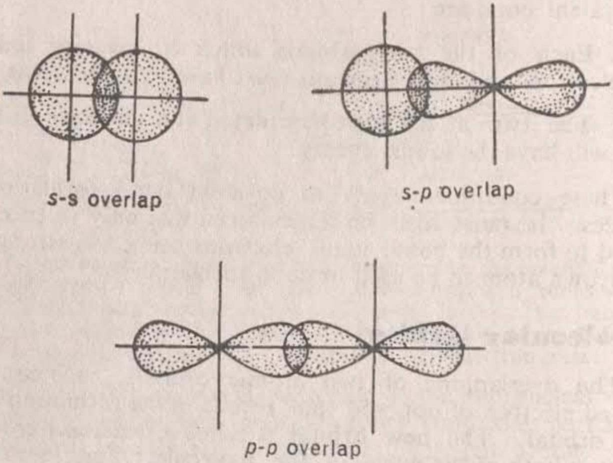

orbitals of separate hydrogen atoms
overlapping of orbitals in the $H_2$ molecule
molecular orbital in $H_2$ molecule

Fig. 19-4. Molecular orbital formation in the $H_2$ molecule.

## 3. Sigma (σ) Bond

A sigma bond is the first bond formed between two atoms in a covalent compound by the *direct*, or *head-on*, or *end-to-end*, overlap of atomic orbitals. In the organic compounds, the formation of sigma (σ) bonds commonly involves the *s* and *p* orbitals in any combination, *i.e.*, *s-s*, *s-p*, and *p-p* combinations. Fig. 19-5 shows the representations of the overlap of (*a*) two *s* orbitals, (*b*) one *s* and one *p* orbital, and (*c*) two *p* orbitals for the formation of sigma (σ) bonds.


*s*-s overlap

*s*-*p* overlap

*p*-*p* overlap

Fig. 19-5. Overlapping of atomic orbitals in the formation of sigma bonds.

A sigma bond is the strongest bond because it has maximum electron density between the nuclei. The molecular orbital corresponding to the sigma bond is cylindrically symmetrical along the axis between the nuclei, and is called a sigma (σ) orbital.

### 4. Pi (π) Bond

A different type of covalent bond is formed by the *side-to-side* overlap of two parallel *p* orbitals (Fig. 19-6). The bond thus formed has a high electron density above and below the internuclear axis, and is called a pi (π) bond. This is a weaker bond than a sigma bond since there is a nodal plane, *i.e.*, zero electron probability density, along the internucleus axis, as shown in Fig. 19-7.

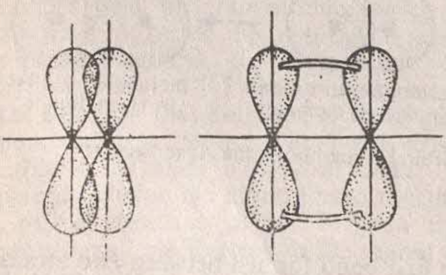


Fig. 19-6. Sideways overlap of two *p* orbitals.

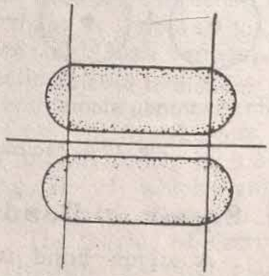


Fig. 19-7. Pi bond with a nodal plane along the internuclear axis.

A pi bond is formed only after a sigma bond has formed by *p-p* overlap; that is, it is the second or third bond between two atoms. When two atoms, A and B, are linked by a sigma bond from *p-p* overlap (Fig. 19-8) each atom is left with two *p* orbitals that are perpendicular to the axis of the $\sigma$ bond. These *p* orbitals are in a position to overlap side-to-side (Fig. 19-9 *a*, *b*). In this way a *double bond* or a *triple bond* is formed between the atoms; one sigma and one pi bond create a double bond, (Fig. 19-9*a*), and one sigma and two pi bonds give rise to a triple bond (Fig. 19-9*b*).

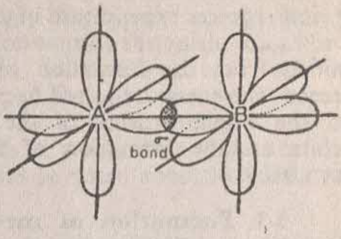


Fig. 19-8. Atoms A and B joined by a $\sigma$ bond from $p_x - p_x$ overlap.

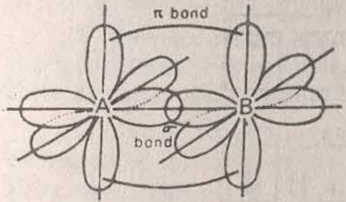


Fig. 19-9. (*a*) A $\pi$ bond is formed by sideway $p_y - p_y$ overlap, giving rise to a double bond between A and B.

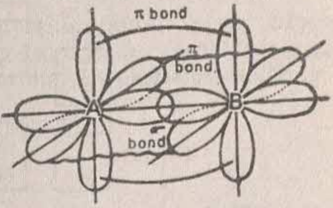
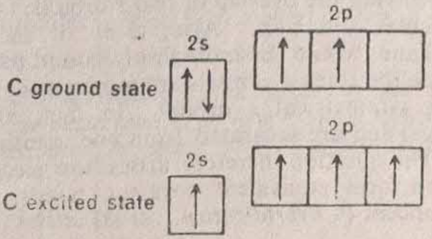


Fig. 19-9. (*b*) A second $\pi$ bond is formed by side ways $p_z - p_z$ overlap giving rise to a triple bond between A and B.

## 5. Covalency of Carbon

The carbon atom (atomic number 6) in the ground state has the electron configuration $1s^2$, $2s^2$, $2p^2$; the configuration for the valence electrons being $2s^2$, $2p_x{}^1$, $2p_y{}^1$, $2p_z{}^0$. In view of only two orbitals containing single or unpaired electrons, one might expect that carbon would be divalent in its compounds*. In the overwhelming majority of its stable compounds, however, carbon is predominantly tetravalent. This is because carbon in the excited state has four orbitals containing single electrons as one of the 2*s* electrons is promoted to the vacant 2*p* orbital. In the pictorial notation—



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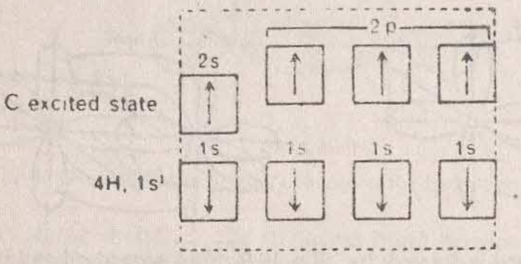
*Since only the orbitals containing unpaired electrons take part in the formation of covalent bond by overlapping with the half-filled orbitals of other atoms.

The $2p$ orbital is at a slightly higher energy level than the $2s$ orbital. Hence, the promotion of an electron from the $2s$ orbital to $2p$ orbital requires expenditure of energy. However, considerable energy is released during the formation of a covalent bond, and the energy gained from the formation of the two 'extra' bonds to carbon far exceeds the energy required to promote a $2s$ electron to the $2p$ level. So the whole process of the promotion of a $2s$ electron to the $2p$ orbital and the formation of four covalent bonds is energetically favourable.

**5-1. Formation of methane molecule, $CH_4$.** The carbon atom in the excited state has four single-electron orbitals—one $2s$ orbital and three $2p$ orbitals. These four orbitals overlap with the spherically symmetrical $1s$ orbitals of four hydrogen atoms to form a molecule of methane.



The electron-dot representation of the formation of methane molecule is :

$$\begin{array}{c}\cdot\\ \cdot\mathrm{C}\cdot\\ \cdot\end{array} + 4\mathrm{H}^{\cdot} \rightarrow \begin{array}{c}\mathrm{H}\\ \cdot\cdot\\ \mathrm{H:C:H}\\ \cdot\cdot\\ \mathrm{H}\end{array} \quad \text{or,} \quad \begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H{-}C{-}H}\\ |\\ \mathrm{H}\end{array},\ \mathrm{CH_4}$$

If the formation of methane involved one $s$ and three $p$ orbitals of carbon atom, the resulting bonds would not all be equivalent. In such a case, three of the C—H bonds would be separated by 90° (the angle separating the $p_x$, $p_y$ and $p_z$ orbitals) while the fourth C—H bond, involving the overlap of two $s$ orbitals (spherical), would have no particular direction. Also, three of the four hydrogen atoms in methane would be more firmly bound to carbon than the fourth one, since the three $p$ orbitals are more strongly directive than the spherically symmetrical $s$ orbital. In fact, all four bonds in $CH_4$ are identical and are separated from one another by an angle to 109° 28′. The question therefore arises how electrons of different energy levels can form equivalent covalent bonds. The answer is given by the concept of *hybridization*.

## 6. Hybridization

Half-filled orbitals, differing only *slightly* in energy, such as the 2*s* and 2*p* orbitals combine together to give equivalent orbitals. The equivalent orbitals formed from different types of orbitals are called *hybrid orbitals* and the process of their formation is termed *hybridization*. The initial shapes of the orbitals undergoing hybridization are altered and hybrid orbitals of a new shape are formed. There are several things which should be noted about hybridization and the hybrid orbitals :

1. Only orbitals of nearly similar energy hybridize, for example, 2*s* and 2*p*; or 3*s*, 3*p*, and 3*d*; or 3*d*, 4*s*, and 4*p*.

2. The number of orbitals that hybridize equals the number of hybrid orbitals formed. For example, if three orbitals of different types hybridize, three hybrid orbitals are formed, if four orbitals hybridize, four hybrid orbitals result.

3. Once an orbital is used for hybridization, it is no longer in the pure form. For example, if one *s* and three *p* orbitals hybridize, there are no longer any pure *s* or *p* orbitals available for bonding.

4. Hybrid orbitals are more elongated on one side of the nucleus than the other (Fig. 19-10). That is they have a highly concentrated electron density on one side. Consequently, the chemical bond formed by hybrid orbitals is stronger than one formed from pure orbitals. Thus, hybridization is linked with an energy gain through the formation of stronger bonds.

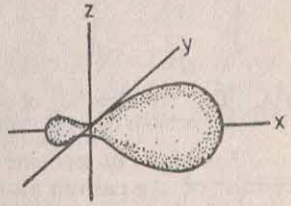


Fig. 19-10. Cross section of *sp* hybrid orbital (on the *x*-axis).

5. The hybrid orbitals in an atom are symmetrically distributed in space so that they are as far apart as possible. Four hybrid orbitals are distributed along the four corners of a regular tetrahedron, with angles of 109° 28′; three hybrid orbitals are in a plane triangle arrangement, with angles of 120°; and two hybrid orbitals are in a linear arrangement, at an angle of 180°.

This fact is of importance in understanding and predicting the geometry of molecules formed by the overlapping of hybrid orbitals.

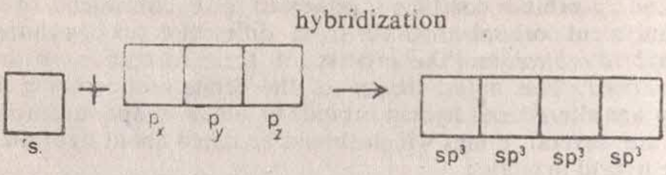
Hybridization may now be defined as follows :

*The merger of dissimilar orbitals of nearly the same energy on an atom to give an equal number of new orbitals identical in shape and energy and distributed in space as far apart as possible is called* **hybridization**.

## 7. $sp^3$ Hybridization

The carbon atom in excited state uses one 2*s* and three 2*p* orbitals for bonding with four hydrogen atoms to form the molecule of methane, $CH_4$. These four orbitals hybridize to give four equivalent

$sp^3$ (pronounced *es-pee-three*) hybrid orbitals, so called in view of the type and number of orbitals combined. Each $sp^3$ orbital has 1/4 *s* character and 3/4 *p* character.



The four $sp^3$ orbitals are directed towards the four corners of a regular tetrahedron and, thus, separated by an angle of 109° 28′ (Fig. 19-11).

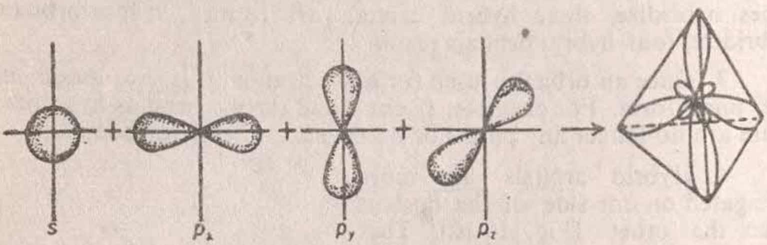


Fig. 19-11. Hybridization of one *s* and three *p* orbitals to give four equivalent $sp^3$ orbitals directed towards the corners of a regular tetrahedron.

*Formation of methane molecule.* Each of the four $sp^3$ hybrid orbitals of the carbon atom (Fig. 19-12, *a*) overlaps with spherically symmetrical 1*s* orbital of a hydrogen atom to form a molecule of methane, $CH_4$ (Fig. 19-12, *b*). Since the orbital overlap occurs in head-on fashion, all the four C—H bonds in the molecule are sigma bonds. These bonds form on angle of 109° 28′ with each other corresponding to the angle between the $sp^3$ hybrid orbitals (Fig. 19-12, *c*). The $sp^3$ orbital, being greatly concentrated in the bond direction, forms stronger bonds than a pure *p* orbital.

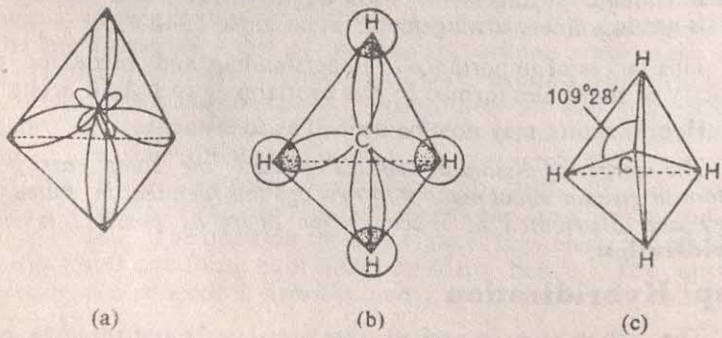


Fig. 19-12. Orbital overlapping of the *s* orbitals of hydrogen atoms and $sp^3$ orbitals of carbon atom in the formation of methane molecule.

*Formation of ethane molecule.* Consider two carbon atoms, each having four $sp^3$ hybrid orbitals. One $sp^3$ orbital of one carbon atom overlaps head-on with an $sp^3$ orbital of the other carbon atom, forming a C—C sigma bond. The remaining three $sp^3$ orbitals on each carbon atom overlap with the 1*s* orbitals hydrogen atoms to form three C—H sigma bonds (Fig. 19-13). The result is a molecule of ethane.

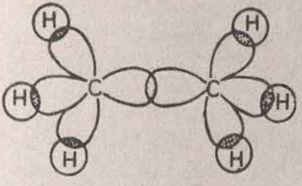
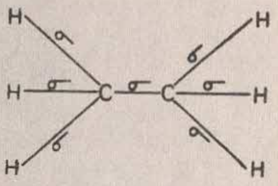


Fig. 19-13(*a*). Orbital overlap in ethane molecule.

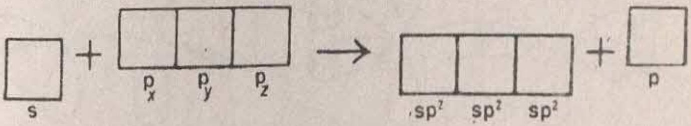


(*b*) Type of bonds in ethane molecule.

The structures of higher alkanes, and of halogen substituted alkanes (*e.g.*, $CH_3Cl$, $CH_2Cl_2$, $C_2H_5Cl$, etc.) can be similarly derived. The C—halogen bond, formed by the head-on over ap of an $sp^3$ orbital of carbon with a *p* orbital of the valence shell ($n.^2$, $np_x^2$, $np_y^2$, $np_z^1$) of the halogen containing single electron, is also a sigma bond.

## 8. sp² Hybridization

The double bond in alkenes, *e.g.*, ethylene $H_2C{=}CH_2$, is constructed of two $sp^2$ hybridized carbon atoms. In the excited carbon atom, two of the three 2*p* orbitals, say $p_x$ and $p_y$ orbitals, hybridize with the 2*s* orbital to give three $sp^2$ *hybridized orbitals.*



The three $sp^2$ hybrid orbitals lie in a plane, disposed at an angle of 120° to one another (Fig. 19-14).

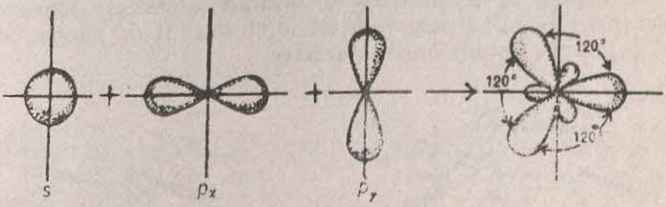


Fig. 19-14. Hybridization of one *s* and two *p* orbitals to give three equivalent $sp^2$ oribitals disposed at an angle of 120° to one another.

The third *p* orbital of the carbon atom, which did not participate in hybridization, is perpendicular to the plane of the hybridized

$sp^2$ orbitals. It is used for bond formation as a pure *p* orbital (Fig. 19-15).

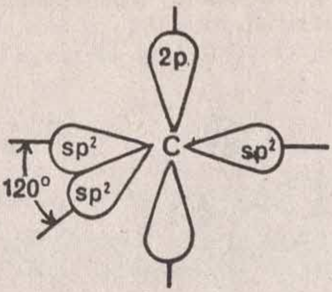


Fig. 19-15. $sp^2$ hybridized carbon atom having 3 $sp^2$ hybrid orbitals and one pure *p* orbital.

*Formation of ethylene molecule*. In ethylene, $H_2C=CH_2$, both carbon atoms are $sp^2$ hybridized. Two $sp^2$ orbitals of each carbon atom overlap *s* orbitals of two hydrogen atoms, whereas the third $sp^2$ orbital of one atom overlaps the third $sp^2$ orbital of the other. Thus, the carbon atoms are joined to the hydrogen atoms and to each other by sigma bonds, with 120° bond angles This is shown in Fig. 19-16.

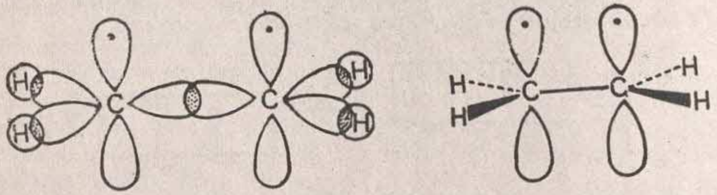
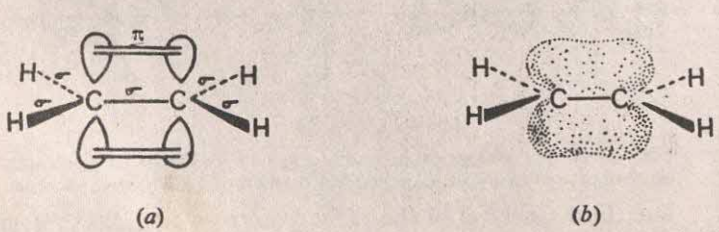


Fig. 19-16. Formation of $\sigma$ bonds in ethylene.

The remaining two *p* orbitals (one for each carbon), which did not participate in hybridization, overlap laterally. This overlap results in a $\pi$ bond between the carbon atoms. It is shown in Fig. 19-17 (*a*) by the double horizontal lines.



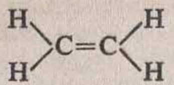
(*a*)

(*b*)

Fig. 19-17(*a*) The *pi* bond in ethylene.

(*b*) The charge clouds ofthe $\pi$ electrons in ethylene.

*Carbon-carbon double bond.* It is obvious that although the conventional structural formula of ethylene,

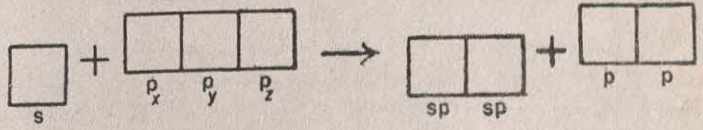


shows both of the bonds of the double bond as equivalent, this is not so. The carbon-carbon double bond consists of two types of bonds : one is a sigma bond formed by the overlapping of two $sp^2$ hybrid orbitals, the other is a *pi* bond formed by the overlapping of two $p$ orbitals. Whereas the $\sigma$ bond is stable and localized, the $\pi$ bond is less stable and the electrons are more mobile in character. This is because the negative charge of the $\pi$ electrons is screened from the attraction of the nucleus by the $\sigma$ electrons as a result of which the $\pi$ electrons are less firmly bound to the carbon atom than the $\sigma$-electrons. In quantitative terms, the bond energy (the energy required to break the bond) is 83 kcal/mole for the sigma bond, while the value for the $\pi$ bond is 64 kcal/mole.

*Planar molecule of ethylene.* The four hydrogen atoms in ethylene and the two carbon atoms attached to the double bond all line in one plane and the $\pi$ electrons are perpendicular to that plane. Hence, the ethylene molecule is planar with 120° bond angles.

## 9. sp Hybridization

The carbon atoms in acetylene, HC≡CH, are *sp* hybridized. That is, the hybrid orbitals are formed from one *s* and one *p* orbital in the excited carbon atom, leaving two pure *p* orbitals.



The two *sp* hybrid orbitals are located at an angle of 180° in a linear arrangement (Fig. 19-18). The two pure *p* orbitals are perpendicular to one another and to the *sp* axis (Fig. 19-19).

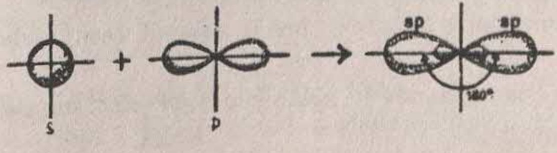


Fig. 19-18. Hybridization of one *s* and one *p* orbitals to give two *sp* hybrid orbitals in a linear arrangement.

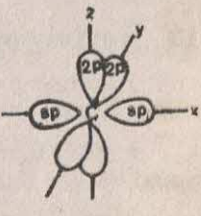


Fig. 19-19. An *sp* hybridized carbon atom (two *sp* hybrid orbitals, two pure *p* orbitals).

*Formation of acetylene molecule.* In acetylene, HC≡CH, one *sp* orbital of one carbon atom overlaps one *sp* orbital of the other, and each remaining *sp* orbital overlaps an *s* orbital of a hydrogen atom, forming stable and localized sigma (σ) bonds (Fig. 19-20). There are then left two pure 2*p* orbitals ($2p_y$, $2p_z$) orbitals on each carbon atom, each orbital containing one electron. They form two sets of parallel *p* orbitals at right angles to each other and also to the σ bond. Sideways overlap of each set gives rise to two pi bonds (Fig. 19-21).

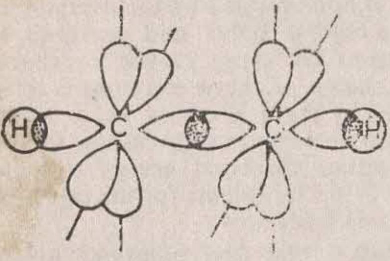
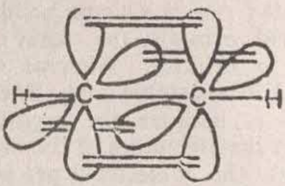


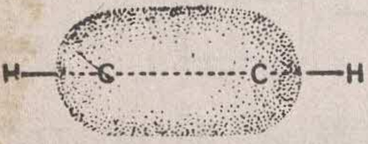
Fig 19-20. Formation of sigma bonds in acetylene.



or, $\mathrm{H} \overset{\sigma}{-} \mathrm{C} \underset{\pi}{\overset{\pi}{\overset{\sigma}{\equiv}}} \mathrm{C} \overset{\sigma}{-} \mathrm{H}$

Fig. 19-21. Pi bonds in acetylene (shown by double horizontal lines).

If the sigma bonds are directed along the *x*-axis, then one π bond is directed along the *y*-axis and the other π bond along the *z*-axis. Thus, carbon-carbon triple bond is made up of one sigma and two pi bonds. There is further overlapping between the π bonds resulting in a charge cloud which is cylindrically symmetrical about the σ bond connecting the nuclei (Fig. 19-22).



or, $\mathrm{H} \overset{\sigma}{-} \mathrm{C} \underset{\pi}{\overset{\pi}{\overset{\sigma}{\equiv}}} \mathrm{C} \overset{\sigma}{-} \mathrm{H}$

Fig. 19-22. Cylindrical π electron cloud of the acetylene molecule.

## 10. Review of Bonding in Organic Compounds

All organic compounds have four bonds around each carbon atom. These bonds could be—

1. four sigma (single) bonds, in which the four electron pairs would occupy four $sp^3$ hybrid orbitals.

2. three sigma bonds and one pi (π), bond, *i.e.*, a double bond, in which case the electron pairs for the sigma bonds would occupy the three $sp^2$ hybridized orbitals, and the unhybridized *p* orbital would overlap sideways with another *p* orbital to form the pi bond, and

3. two sigma bonds and two pi bonds, *i.e.*, a triple bond; the electron pairs of sigma bonds occupy the two *sp* hybrid orbitals, and the two unhybridized *p* orbitals overlap sideways with parallel *p* orbitals on another atom to for two pi bonds.

In the $sp^3$ bonding, the molecule has a tetrahedral structure with an angle of 109°28′ between the bonds. In $sp^2$ structure, the shape is a plane triangle and the bond angles are 120°. In the *sp* structure, the bonds are at an angle of 180°, giving a linear structure.

## Questions

1. Explain the concept of orbital overlap in covalent bonding.

2. What are the essential conditions for orbital overlap in the formation of covalent bond ?

3. What is a molecular orbital ? Explain with the example of hydrogen molecule.

4. Explain the formation of sigma bond and pi bond with the help of suitable diagrams. Which of these two bonds is stronger and why ?

5. Explain the reason why carbon atom having only two half-filled orbitals in the valence shell is predominantly tetravalent.

6. (*a*) What kinds of orbitals undergo hybridization ? If three different types of orbitals hybridize, how many hybrid orbitals will result ?

(*b*) Describe the shape of a hybrid orbital and draw a diagram for it.

(*c*) How are the hybrid orbitals in an atoms distributed in space ?

7. Explain the reason why

(*a*) the bonds formed by hybrid orbitals are stronger than those formed by pure orbitals,

(*b*) all the C—H bonds in $CH_4$ molecule are equivalent,

(*c*) $CH_4$ molecule has a tetrahedral structure, ethylene molecule a planar structure, and acetylene molecule a linear structure ?

8. Describe the bonding in each of the following molecules (including type of hybridization, types of bonds, and bond angles) :

(*a*) $CH_4$ (*b*) $C_2H_6$ (*c*) $C_2H_4$ (*d*) $C_2H_2$.

Draw a sketch for bonding in each of these molecules.

9. Draw sketches for (*a*) $sp^3$ hybridized carbon atom, (*b*) a $sp^2$ hybridized carbon atom, and (*c*) a *sp* hybridized carbon atom.

10. How many sigma bonds and pi bonds are there in the following molecules :

(*a*) $CH_4$ (*b*) $C_2H_5Cl$ (*c*) $C_2H_4$ (*d*) $C_2H_2Cl_2$ ?

## Key

7. (*a*) A hybrid orbital has a highly concentrated electron density on one side.

(*b*) Because all the four C—H bonds are formed by the overlap of 1*s* orbitals of hydrogen atoms with four equivalent $sp^3$ hybrid orbitals of the carbon atom.

(*c*) The four $sp^3$ hybrid orbitals in methane are disposed tetrahedrally, the three $sp^2$ hybrid orbitals in ethylene are in a plane triangle, while the two *sp* hybrid orbitals in acetylene are in a linear arrangement.

8. (*a*) $sp^3$ hybridization, sigma bonds only, bond angle 109°28′,

(*b*) the same as in (*a*),

(*c*) $sp^2$ hybridization, sigma and pi bonds, bond angle 120° between sigma bonds,

(*d*) $sp$ hybridization, sigma and pi bonds, bond angle 180° between sigma bonds.

10. (*a*) Only four sigma bonds (C—H).

(*b*) Only seven sigma bonds (six C—H bonds and one C—C bond).

(*c*) Five sigma bonds (four C—H bonds and one C—C bond); one pi bond between the two carbon atoms.

(*d*) three sigma bonds (two C—H bonds and one C—C bond); two pi bonds between the two carbon atoms.

□ □

# 20

# Halogen Derivatives of Alkanes

## (Ethyl Chloride, Ethyl Bromide, Chloroform, Iodoform)

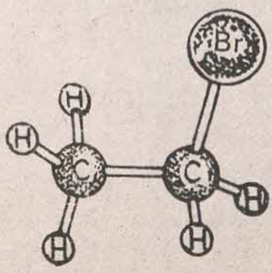
Halogen derivatives of alkanes are compounds which may be regarded as products of the replacement of one or several hydrogen atoms in the alkane molecule by halogen atoms. Depending upon the number of hydrogen atoms replaced by the halogen, these may be monohalogen, dihalogen, trihalogen, and in general, polyhalogen derivatives. Of these the monohalogen and trihalogen derivatives are more important. All halogen derivatives are artificially prepared substances and do not occur in nature.

The monohalogen derivatives of alkanes form a homologous series with the general formula $C_nH_{2n+1}X$, or, RX, where X may be F, Cl, Br, or I. They are named as alkyl halides, *e.g.*, ethyl chloride, ethyl bromide, etc., or in the I.U.P.A.C. system as haloalkanes, *e.g.*, chloroethane, bromoethane, etc. The lower alkyl halides are gases, the ones following are liquids, and the higher still are solids. The boiling points and densities of alkyl halides rise with the increase in the atomic weight of the halogen in the molecule. Chemically, the alkyl halides rank among highly reactive organic substances. They readily exchange the halogen atom for various groups and are, therefore, used for numerous organic syntheses.

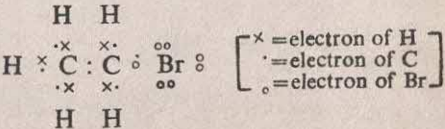
The most important trihalogen derivatives of alkanes are chloroform and iodoform, both of which are the trihalides of methane.

## 1. Alkyl Halides

Among the alkyl halides, the ethyl halides (ethyl chloride, ethyl bromide, and ethyl iodide) are by far the most important. These are derived from ethane by the replacement of one of its hydrogen atoms by a halogen atom (X). The ball and stick model of ethyl bromides and its electronic formula are given below for illustration :



Ball and stick model of ethylene bromide.



$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & \cdot\times & & \times\cdot & & \circ\circ \\ \mathrm{H} & \overset{\times}{\cdot} & \mathrm{C} & : & \mathrm{C} & \overset{\circ}{\cdot} & \mathrm{Br}\ \overset{\circ}{\circ} \\ & & \cdot\times & & \times\cdot & & \circ\circ \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

Electronic formula of ethyl bromide.

**1-1. General Methods of Preparation**. Alkyl halides, *i.e.*, the monohalogen derivatives of alkanes are usually made by the following general methods :

1. *By direct halogen substitution in the alkane.*

$$\underset{\text{ethane}}{C_2H_6} + Cl_2 \longrightarrow \underset{\text{ethyl chloride}}{C_2H_5Cl} + HCl$$

$$\underset{\text{ethane}}{C_2H_6} + Br_2 \longrightarrow \underset{\text{ethyl bromide}}{C_2H_5Br} + HBr$$

The reactions of chlorination and bromination proceed under the influence of light. However, the method is of little practical value for the preparation of particular alkyl halides since the reaction cannot be controlled and results in a complex mixture of various mono-, di-, tri-, etc. halogen substitution products.

2. *By the addition of hydrogen halides* (*HX*) *to olefins.*

$$\underset{\text{ethylene}}{CH_2{=}CH_2} + HCl \rightarrow \underset{\text{ethyl chloride}}{CH_3.CH_2Cl}$$

$$\underset{\text{ethylene}}{CH_2{=}CH_2} + HBr \rightarrow \underset{\text{ethyl bromide}}{CH_3.CH_2Br}$$

This method, too, is of little practical value and is rarely used.

3. *By the action of hydrogen halides* (*HX*) *on alcohols*. Hydrogen iodide reacts most readily, while hydrogen bromide and hydrogen chloride require higher temperatures and the use of concentrated sulphuric acid or anhydrous zinc chloride. These substances shift the following equilibrium to the right by the removal of the water formed :

$$\underset{\text{alcohol}}{R.OH} + HX \rightleftharpoons \underset{\text{alkyl halide}}{RX} + H_2O$$

As a modification, alcohol is heated with a mixture of concentrated sulphuric acid (in excess) and potassium halide, *e.g.*, potassium bromide for the preparation of an alkyl bromide.

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} + HCl \xrightarrow{\substack{\text{conc.} \\ H_2SO_4}} \underset{\text{ethyl chloride}}{C_2H_5Cl} + H_2O$$

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} + HBr \xrightarrow{\substack{\text{conc.} \\ H_2SO_4}} \underset{\text{ethyl bromide}}{C_2H_5Br} + H_2O$$

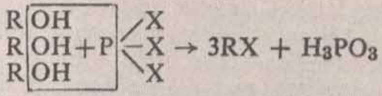
4. *By the action of a phosphorus trihalide* (*$PX_3$*) *on alcohols.*

$$\underset{\text{alcohol}}{3ROH} + PX_3 \rightarrow \underset{\text{alkyl halide}}{3RX} + H_3PO_3$$

$$\underset{\text{ethyl alcohol}}{3C_2H_5OH} + PCl_3 \rightarrow \underset{\text{ethyl chloride}}{3C_2H_5Cl} + H_3PO_3$$

$$\underset{\text{ethyl alcohol}}{3C_2H_5OH} + PBr_3 \rightarrow \underset{\text{ethyl bromide}}{3C_2H_5Br} + H_3PO_3$$

The equation may be explained as—



$$\begin{array}{l} R\boxed{OH} \\ R\boxed{OH}+P\!\begin{array}{l}/X\\-X\\\backslash X\end{array} \\ R\boxed{OH} \end{array} \rightarrow 3RX + H_3PO_3$$

In practice phosphorus bromide and iodide are made in situ by adding bromine and iodine respectively to a mixture of red phosphorus and alcohol.

Alkyl chlorides can often be conveniently made by the action of thionyl chloride on alcohols.

$$\underset{\text{alcohol}}{ROH} + \underset{\text{thionylchloride}}{SOCl_2} \rightarrow \underset{\text{alkyl chloride}}{RCl} + SO_2\uparrow + HCl\uparrow$$

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} + SOCl_2 \rightarrow \underset{\text{ethyl chloride}}{C_2H_5Cl} + SO_2\uparrow + HCl\uparrow$$

**1-2. Laboratory preparation of ethyl chloride** (*chloroethane*). Ethyl chloride can be conveniently prepared by the Groves process. Dry hydrogen chloride is passed into a mixture of absolute alcohol and anhydrous chloride, which acts not only as a catalyst but also as a dehydrating agent.

$$C_2H_5OH + HCl \overset{ZnCl_2}{\rightleftharpoons} C_2H_5Cl + H_2O$$

When the alcohol has been saturated with hydrogen chloride, the mixture is heated under reflux on a water-bath. The ethyl chloride vapour issuing from the top of the condenser is passed successively through wash bottles containing respectively water to remove hydrogen chloride, sodium carbonate solution to remove alcohol, and concentrated sulphuric acid to remove moisture. The pure ethyl chloride is then condensed in a U-tube surrounded by freezing mixture.

**1-3. Laboratory preparation of ethyl bromide** (*bromoethane*). Ethyl bromide is prepared in the laboratory by heating absolute alcohol with concentrated sulphuric acid (in excess) and potassium bromide, using the apparatus as shown in Fig. 20-1. The sulphuric acid reacts with potassium bromide liberating anhydrous hydrogen bromide in situ; it also serves as a catalyst and improves the yield by removing the water liberated in the reaction.

$$KBr + H_2SO_4 \rightarrow KHSO_4 + HBr$$

$$C_2H_5OH + HBr \rightleftharpoons C_2H_5Br + H_2O$$

The sulphuric acid is slowly added to the alcohol in the flask with continual shaking. Then some coarsely ground potassium bromide is added and the flask is immediately connected to a condenser. The flask is heated over a sand bath when ethyl bromide distils over and collects under the layer of water in the receiver. The product is impure containing water, bromine, alcohol, and also dissolved sulphur dioxide and hydrogen bromide. It is separated by means of a separating funnel and shaken with successive quantities of sodium carbonate solution to neutralize the acids. It is again separated, washed with water to remove residual carbonate, and then dried with anhydrous calcium chloride. The ethyl bromide thus purified is distilled over a water-bath and the fraction distilling over between 35°C and 40°C is collected. It is reasonably pure ethyl bromide with only traces of ether as an impurity.

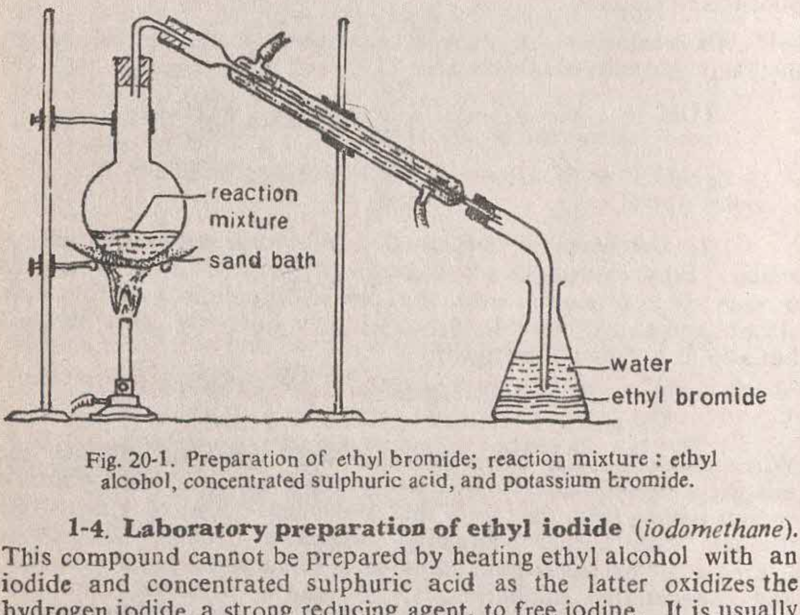


Fig. 20-1. Preparation of ethyl bromide; reaction mixture : ethyl alcohol, concentrated sulphuric acid, and potassium bromide.

**1-4. Laboratory preparation of ethyl iodide** (*iodomethane*). This compound cannot be prepared by heating ethyl alcohol with an iodide and concentrated sulphuric acid as the latter oxidizes the hydrogen iodide, a strong reducing agent, to free iodine. It is usually prepared, therefore, by heating ethyl alcohol with red phosphorus and iodine, phosphorus tri-iodide being produced in situ.

$$2P + 3I_2 \rightarrow 2PI_3 \text{ (phosphorus tri-iodide)}$$

$$3C_2H_5OH + PI_3 \rightarrow 3C_2H_5I + H_3PO_3$$

Alcohol and red phosphorus are mixed in a flask fitted with an upright reflux condenser. Iodine crystals are added, a little at a time, the flask being cooled if necessary. The mixture is heated on a boiling water-bath for about an hour. The condenser is then changed from the reflux to the normal position when ethyl iodide distils over. The product is impure containing water, alcohol, hydrogen iodide, and a little iodine which gives it a yellowish brown colour. It is separated from the water, and washed first with sodium carbonate solution and then with water. Finally it is dried with anhydrous calcium chloride, and distilled on a water-bath. The fraction distilling over between 68°C and 73°C is pure ethyl iodide.

## 2. Physical Properties of Alkyl Halides

Methyl chloride, methyl bromide, and ethyl chloride are gases at ordinary temperatures, b.p. − 23·7°C, 3·5°C, and 12·3°C respectively. Higher members of this homologous series are liquids, only a few being solids. The melting points, boiling points, and densities increase as in other homologous series with increase in molecular weight. The lower alkyl halides have a characteristic sweetish odour. The alkyl halides are insoluble in water but dissolve readily in alcohol and ether.

## 3. Reactions of Alkyl Halides

The alkyl halides are, generally speaking, highly reactive individuals. They will react with a variety of reagents, readily exchanging the halogen atom for other substituent groups. The reactions are usually carried out by boiling the reaction mixture. The iodides are the most reactive and the chlorides the least, but these are only differences of degree and all alkyl halides are essentially similar chemically. Their principal reactions are as follows :

**1. Hydrolysis.** Alkyl halides are slowly hydrolysed to *alcohols* by boiling water.

$$\underset{\text{ethyl bromide}}{C_2H_5\boxed{Br + H}OH} \rightleftharpoons \underset{\text{ethyl alcohol}}{C_2H_5OH} + HBr$$

The hydrolysis occurs rapidly by hot aqueous solutions of alkalis which neutralize the halogen hydride (*e.g.*, HBr) and make the reaction irreversible.

$$C_2H_5Br + NaOH \rightarrow C_2H_5OH + NaBr$$

Hydrolysis of alkyl halides rapidly occurs when these are boiled with a suspension of silver oxide in water.

$$Ag_2O + H_2O \rightleftharpoons 2AgOH$$

$$C_2H_5Br + AgOH \rightarrow C_2H_5OH + AgBr\downarrow$$

**2. Reduction.** When treated with nascent hydrogen (*e.g.*, by means of a zinc-copper couple and water or ethyl alcohol, sodium and ethyl alcohol, etc.), alkyl halides are reduced to the corresponding *alkanes*, *e.g.*, ethyl halides to ethane.

$$\underset{\text{ethyl bromide}}{C_2H_5Br} + 2[H] \rightarrow \underset{\text{ethane}}{C_2H_6} + HBr$$

**3. Wurtz reaction.** When a solution of an alkyl halide in dry ether is heated with metallic sodium it is converted into an *alkane* containing double the number of carbon atoms in the alkyl halide molecule. Thus, ethyl halides give butane, $C_4H_{10}$.

$$\underset{\text{ethyl bromide}}{C_2H_5\boxed{Br + 2Na + Br}}\underset{\text{ethyl bromide}}{C_2H_5} \rightarrow \underset{\text{butane}}{C_2H_5.C_2H_5} + 2NaBr$$

*i.e.*, $$2C_2H_5Br + 2Na \rightarrow C_4H_{10} + 2NaBr$$

Such reactions involving the removal of the halogen by sodium and the combination of the resulting free alkyl radicals (*e.g.*, $C_2H_5-$ in the case of ethyl halides) are known as Wurtz reaction or Wurtz synthesis.

**4. Williamson's reaction.** Alkyl halides react with an alcoholic solution of sodium alkoxide (sodium derivatives of an alcohol, RONa) on warming giving *ethers*. For instance, ethyl bromide reacts with sodium ethoxide ($C_2H_5ONa$) to give diethyl ether.

$$\underset{\text{ethyl bromide}}{C_2H_5}\boxed{Br + Na}\underset{\text{sodium ethoxide}}{OC_2H_5} \rightarrow \underset{\text{diethyl ether}}{C_2H_5.O.C_2H_5} + NaBr$$

The same products, *viz.*, ethers, are obtained with dry silver oxide.

$$\underset{\text{ethyl bromide}}{2C_2H_5Br} + Ag_2O \rightarrow \underset{\text{diethyl ether}}{C_2H_5O.C_2H_5} + 2AgBr$$

**5. Dehydrohalogenation.** When an alkyl halide is heated with potassium hydroxide dissolved in alcohol (alcoholic potash), it loses a molecule of hydrogen halide to give an alkene. Thus, ethyl halides give ethylene.

$$\underset{\text{ethyl bromide}}{C_2H_5Br} + KOH \rightarrow \underset{\text{ethylene}}{C_2H_4} + KBr + H_2O$$

Higher alkyl halides give a good yield of alkene, but in the case of ethyl halides ethylene is formed only in traces, the main product being diethyl ether. This is because the solution of potassium hydroxide in alcohol contains a high concentration of potassium ethoxide ($C_2H_5OK$) which reacts with alkyl halide to produce the ether.

$$\underset{\text{ethyl bromide}}{C_2H_5}\boxed{Br + K}\underset{\text{potassium ethoxide}}{OC_2H_5} \longrightarrow \underset{\text{diethyl ether}}{C_2H_5.O.C_2H_5} + KBr$$

**6. Reaction with potassium cyanide.** When an alkyl halide is boiled with an alcoholic solution of potassium cyanide, corresponding *alkyl cyanide* is formed. For example,

$$\underset{\text{ethyl bromide}}{C_2H_5}\boxed{Br + K}CN \rightarrow \underset{\text{ethyl cyanide}}{C_2H_5.CN} + KBr$$

Alkyl cyanides can be used to prepare the following classes of compounds :

(*i*) *Acid amides* by partial hydrolysis with alkaline hydrogen peroxide.

$$\underset{\text{ethyl cyanide}}{C_2H_5.CN} + H_2O \xrightarrow{\text{alk. } H_2O_2} \underset{\text{propionamide}}{C_2H_5.CO.NH_2}$$

(*ii*) *Carboxylic acids* by hydrolysis with mineral acids or alkalis.

$$\underset{\text{ethyl cyanide}}{C_2H_5.CN} + 2H_2O \rightarrow \underset{\text{propionic acid}}{C_2H_5.COOH} + NH_3$$

(*iii*) *Primary amines* by reduction with nascent hydrogen (from sodium and alcohol, for instance).

$$\underset{\text{ethyl cyanide}}{C_2H_5.CN} + 4[H] \rightarrow \underset{\text{propylamine}}{C_2H_5.CH_2.NH_2}$$

**7. Reaction with silver cyanide.** When alkyl halides are heated with aqueous alcoholic silver cyanide, *alkyl isocyanides* are formed as the main product (isomeric cyanides being formed in traces). For example,

$$\underset{\text{ethyl bromide}}{C_2H_5\boxed{Br + Ag}CN} \rightarrow \underset{\text{ethyl isocyanide}}{C_2H_5.NC} + AgBr$$

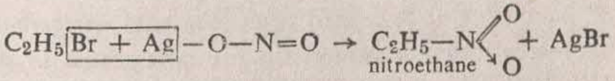
This reaction is explained on the basis of silver cyanide being a covalent compound with a chain structure in which the silver atoms are linked directly to both carbon and nitrogen atoms. Potassium cyanide, on the other hand, is largely an ionic compound.

**8. Reaction with potassium nitrite.** When an alkyl halide is heated with an aqueous alcoholic solution of potassium nitrite, an *alkyl nitrite*, $R-O-N=O$, is obtained as the main product. For example,

$$\underset{\text{ethyl bromide}}{C_2H_5\boxed{Br + K}}\underset{\text{potassium nitrite}}{-O-N=O} \rightarrow \underset{\text{ethyl nitrite}}{C_2H_5-O-N=O} + KBr$$

Some nitroethane is also formed in this reaction.

**9. Reaction with silver nitrite.** When an alkyl halide is heated with an aqueous alcoholic solution of silver nitrite, a *nitroparaffin* is formed as the main product; alkyl nitrite is also formed in traces. For example,



$$C_2H_5\boxed{Br + Ag}-O-N=O \rightarrow \underset{\text{nitroethane}}{C_2H_5-N\begin{matrix}\nearrow O\\ \searrow O\end{matrix}} + AgBr$$

**10. Reaction with the silver salt of a carboxylic acid.** When alcoholic solutions of a silver salt of a carboxylic acid is warmed with an alkyl halide, an *ester* is formed. Thus ethyl bromide and silver acetate, $CH_3.COOAg$, interact to give ethyl acetate.

$$\underset{\text{ethyl bromide}}{C_2H_5\boxed{Br + Ag}}\underset{\text{silver acetate}}{OOC.CH_3} \rightarrow \underset{\text{ethyl acetate}}{C_2H_5.OOC.CH_3} + AgBr$$

**11. Reaction with ammonia.** When an alkyl halide is heated with an alcoholic solution of ammonia under pressure in a sealed tube, the salt of a primary amine (*e.g.*, $C_2H_5.NH_2.HBr$) is formed as the first product. Thus,

$$C_2H_5Br + NH_3 \rightarrow C_2H_5.NH_2 + HBr$$

However, the reaction does not stop here, and the salts of secondary and tertiary amines and even quaternary ammonium compounds are also formed.

$$C_2H_5.NH_2 + C_2H_5Br \longrightarrow \underset{\text{diethylamine}}{(C_2H_5)_2NH} + HBr$$

$$(C_2H_5)_2NH + C_2H_5Br \longrightarrow \underset{\text{triethylamine}}{(C_2H_5)_3N} + HBr$$

$$(C_2H_5)_3N + C_2H_5Br \longrightarrow \underset{\substack{\text{tetraethylammonium}\\ \text{bromide (quaternary compound)}}}{(C_2H_5)_4NBr}$$

**12. Reaction with zinc (Frankland's Reaction).** The action of zinc on the alkyl halides produces dialkyls zinc, *e.g.*, diethyl zinc.

$$\underset{\text{ethyl bromide}}{2C_2H_5Br} + 2Zn \rightarrow \underset{\text{diethyl zinc}}{(C_2H_5)_2Zn} + ZnBr_2$$

**13. Reaction with magnesium.** Alkyl halides in the presence of dry ether combine with magnesium, giving alkyl magnesium halides, called Grignard reagents after the name of their French discoverer Victor Grignard.

$$\underset{\text{ethyl bromide}}{.C_2H_5Br} + Mg \xrightarrow{\text{ether}} \underset{\text{ethyl magnesium bromide}}{C_2H_5.MgBr}$$

**14. Combustibility.** Lower alkyl halides are combustible and burn with green edged flames.

## 4. Uses of Alkyl Halides

1. The alkyl halides are widely used in *organic syntheses*. They serve as the starting material in the preparation of several classes of organic compounds (alkanes, alkenes, ethers, esters, amines, Grignard reagents, etc.).

2. Methyl chloride, $CH_3Cl$, and ethyl chloride, $C_2H_5Cl$, are used as *alkylating agents*, *i.e.*, for replacing an acidic hydrogen atom by an alkyl group, *e.g.*, in the manufacture of silicones.

3. Methyl chloride is used as an industrial *refrigerant*.

4. Methyl bromide is used as a fire extinguisher in aircraft and, owing to its toxicity, as a powerful *fumigant* for pests in stored fruit or grain.

5. Ethyl chloride is used as a *local anaesthetic* for minor operations since it evaporates rapidly (b.p. 13·1°C) on the skin, causing the sharp cooling of the adjacent flesh. It is also used on a large scale for making tetraethyl lead, an *antiknock agent* used as petrol additive, from a sodium-lead alloy.

$$\underset{\text{ethyl chloride}}{4C_2H_5Cl} + Na_4Pb \rightarrow \underset{\text{tetraethyl lead}}{(C_2H_5)_4Pb} + 4NaCl$$

Ethyl chloride is also used in the production of the important plastic ethyl cellulose.

## 5. Mechanisms of Substitution Reactions of Alkyl Halides

The substitution reactions of the alkyl halides are characterized by the replacement of the halogen atom (X) attached to the carbon atom by another substituent. In these reactions the halogen atom takes with it the bonding pair of electrons constituting the C—X bond, and is eliminated as the anion $X^-$. Obviously, the incoming substituent must be such as can contribute one unshared pair of electrons required in the formation of the new covalent bond with the carbon atom linked to the halogen atom in the alkyl halide. The incoming substituent, —B, may thus be an anion such as $OH^-$, $CN^-$, etc., or an electrically neutral base, such as the ammonia molecule with a pair of unshared electrons, $:NH_3$.

$$R-X + OH^- \rightarrow R-OH + X^-$$

Since the substituents are electron donors or *nucleophiles* ("nucleus seeking"), the substitution reactions of alkyl halides are described as *nucleophilic substitution*, denoted by the symbol $S_N$. Two reaction mechansims are possible in the displacement of the halogen, and the mechanism which applies to a particular reaction is determined chiefly by the character of the group R. Corresponding to the two reaction mechanisms, there are two types of substitution reactions, the $S_N2$ reactions and the $S_N1$ reactions.

**5-1. The $S_N2$ reaction.** The symbol $S_N2$ means substitution of the nucleophilic type by a bimolecular process, the *S* in the symbol standing for substitution, the N for nucleophilic, and the 2 for bimolecular. The alkaline hydrolysis of alkyl bromides, *e.g.*, methyl bromide is a typical example of the $S_N2$ reactions.

$$\underset{\text{methyl bromide}}{CH_3Br} + OH^- \xrightarrow{\text{base, } H_2O} \underset{\text{methyl alcohol}}{CH_3OH} + Br^-$$

Both reactants participate in the primary process, which is initiated by the nucleophile $OH^-$ approaching the $CH_3Br$ molecule. It is, therefore, a *bimolecular* reaction. The reaction rate being proportional to the concentration of both the hydroxide ion and the methyl bromide, it is a *second-order reaction*. The mechanism for the reaction* is as follows :

*a.* The hydroxide ion approaches the carbon atom in methyl bromide molecule, which carries a fractional positive charge owing to the polarity of the C—Br bond, from the side opposite the bromine.

*b.* As the hydroxide ion approaches closer and closer to the carbon atom, the attraction between the carbon and the oxygen atoms continuously increases and that between the carbon and bromine atoms correspondingly decreases. As the process continues the two attractions eventually become equal, and an intermediate *transition state* is formed.

*c.* Since the hydroxide ion is a better electron donor and possesses greater tendency to form a covalent bond than chlorine,

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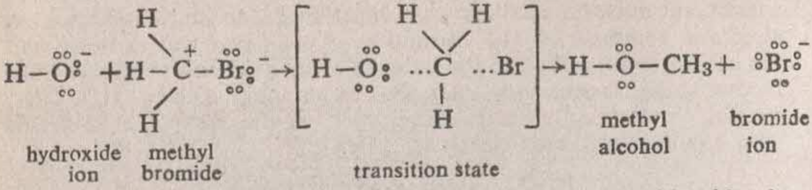
*By *reaction mechanism,* we mean a stepwise account of a reaction in terms of the sequence and manner in which the bonds are broken and formed.

the oxygen atom forms a covalent link with the carbon displacing the bromine as the bromide ion*. In this process, the C—O *bond formation* and C—Br *bond rupture* occur simultaneously.



The formation of the transition state requires considerably less activation energy than a preceding rupture of the C—Br bond.

The mechanism of $S_N2$ reaction may thus be described as a *rearward nucleophilic attack of an electron donor upon the carbon atom of the alkyl halide with displacement of halogen as the anion.*

The hydrolysis of an alkyl halide to alcohol also occurs with nucleophilic water, but the rate is considerably lower than with alkalis. This is because the hydroxide ion is a stronger nucleophile than water.

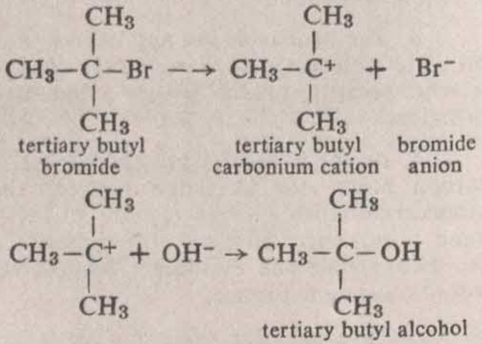
**5-2. The $S_N1$ reaction.** The symbol $S_N1$ means substitution of the nucleophilic type by a unimolecular process. In the $S_N1$ reaction the C—X bond of the alkyl halide undergoes a slow ionization before the carbon atom combines with the nucleophile (*e.g.*, $OH^-$). Since this rate-controlling step involves only one molecule, the reaction is essentially unimolecular. The hydrolysis of tertiary butyl bromide with alkalis is a typical example of $S_N1$ reaction. It proceeds in two steps :

*a.* Tertiary butyl bromide undergoes a slow ionization, giving the tertiary butyl carbonium cation and a bromide anion. This is the rate-determining step.

*b.* The carbonium cation combines with the nucleophile $OH^-$ in a secondary reaction which is very fast.

*Step 1*
*Slow ionization*

*Step 2*
*Fast addition*



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Br \longrightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^+}} + Br^-$$

$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^+}} + OH^- \rightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OH$$

---

*The three hydrogen atoms attached to the carbon atom in the transition state are arranged in one plane at an angle of 120°. The attacking hydroxide ion and the bromine atom being displaced move along a line perpendicular to this plane.

The reaction rate is proportional to the concentration of the alkyl halide only and is independent of the concentration of the $OH^-$ ions. It is, therefore, a first-order reaction.

The $S_N^1$ reaction occurs when the C$-$X bond in the alkyl halide is highly polar and the carbonium ion formed is particularly stable.

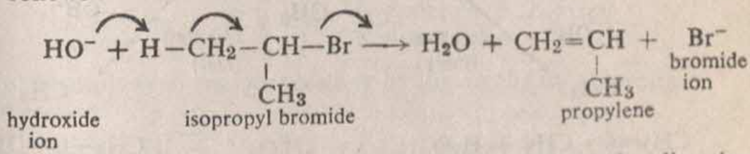
## 6. Mechanisms of Elimination Reactions of Alkyl Halides

When a higher alkyl halide is boiled with alcoholic potash, hydrogen and halogen from adjacent carbon atoms are removed as hydrogen halide, and an alkene is formed. For example, propyl bromide ($C_3H_7Br$) gives propylene ($C_3H_6$)

$$\underset{\text{propyl bromide}}{CH_3.CH_2.CH_2Br} + KOH(\text{alc.}) \rightarrow \underset{\text{propylene}}{CH_3.CH{=}CH_2} + KBr + H_2O$$

Such reactions are called **elimination** reactions. These may proceed by bimolecular mechanism, symbolized by $E_2$, or by unimolecular mechanism, symbolized by $E_1$.

**6-1. The $E_2$ reaction.** This is similar to the $S_N^2$ reaction except that the nucleophile (*e.g.*, $OH^-$) approaches the hydrogen atom instead of the carbon. As applied to the formation of propylene from isopropyl bromide by the action of alcoholic potash, the manner in which the bonds are made and broken may be shown as follows :

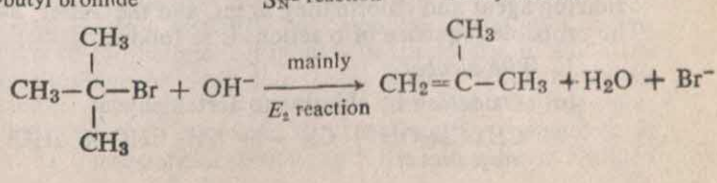


$$\underset{\text{hydroxide ion}}{HO^-} + \underset{\text{isopropyl bromide}}{H-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-Br} \longrightarrow H_2O + \underset{\text{propylene}}{CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{CH}}} + \underset{\text{bromide ion}}{Br^-}$$

In the above representation, the curved arrows indicate the direction of movement of electrons.

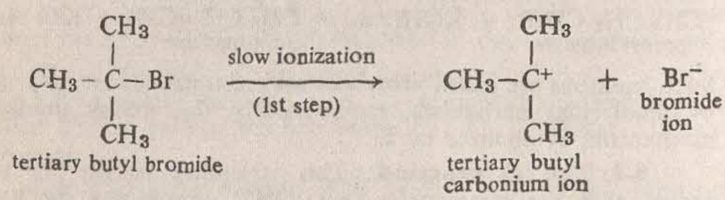
The $E_2$ and $S_N^2$ reactions are always competitive and a concentrated alkali solution must be used for the $E_2$ reaction to predominate because only a strong base has the ability to remove the hydrogen halide from an alkyl halide. In general, $S_N^2$ reaction predominates over the $E_2$ reactions with primary halides, while for tertiary halides the opposite holds true. For example, *n*-butyl bromide yields mainly *n*-butyl alcohol and only traces of butylene; tertiary butyl bromide gives almost exclusively the alkene isobutylene.

$$\underset{n\text{-butyl bromide}}{CH_3.CH_2.CH_2.CH_2Br} + OH^- \xrightarrow[S_N^2\text{ reaction}]{\text{mainly}} \underset{n\text{-butyl alcohol}}{CH_3.CH_2.CH_2.CH_2OH} + Br^-$$

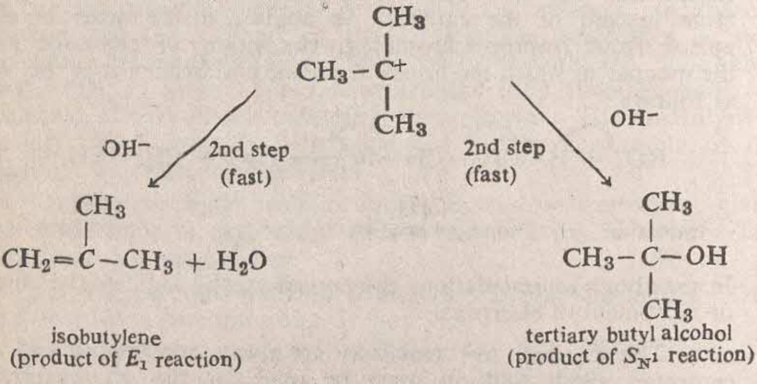


$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Br + OH^- \xrightarrow[E_2\text{ reaction}]{\text{mainly}} CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_3 + H_2O + Br^-$$

**6-2. The $E_1$ reaction.** The $E_1$ reaction is completed in two steps. The first step is the slow ionization of the alkyl halide into the **carbonium** ion and the halide ion, and this is the rate-determining step. The second step involves the removal of a proton from the carbonium ion by the hydroxide ion, which proceeds very rapidly. Thus, with the stepwise loss of the halogen and hydrogen an alkene is produced. However, the carbonium ion produced in the first step may also combine with the hydroxide ion to give an alcohol, in which case it is the $S_N1$ reaction. Obviously, just as the $E_2$ and $S_N2$ reactions are competitive, the $E_1$ reaction always competes with the $S_N1$ reaction. The hydrolysis of tertiary butyl bromide, for example, gives the alkene isobutylene by the $E_1$ reaction and isobutyl alcohol by the $S_N1$ reaction.



$$(CH_3)_3C{-}Br \xrightarrow[\text{(1st step)}]{\text{slow ionization}} (CH_3)_3C^+ + Br^-$$



$$(CH_3)_3C^+ \xrightarrow[\text{(fast)}]{OH^-,\ \text{2nd step}} CH_2{=}C(CH_3){-}CH_3 + H_2O$$

$$(CH_3)_3C^+ \xrightarrow[\text{(fast)}]{OH^-,\ \text{2nd step}} (CH_3)_3C{-}OH$$

## CHLOROFORM, $CHCl_3$

## 7. Preparation of Chloroform

**7-1. Laboratory preparation.** Chloroform is prepared in the laboratory by the action of a hypochlorite, such as bleaching powder (it is calcium chloride hypochlorite) on alcohol, acetaldehyde, or acetone. The hypochlorite behaves virtually as if it were composed of chlorine and the alkaline hydroxide, the former serving both as oxidizing agent and chlorinating agent, and the latter as an alkali. The probable sequence of reactions is as follows :

1. *With alcohol*

(*a*) Oxidation by chlorine to acetaldehyde –

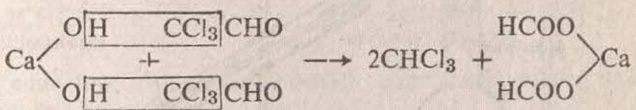
$$\underset{\text{ethyl alcohol}}{CH_3.CH_2OH} + Cl_2 \longrightarrow \underset{\text{acetaldehyde}}{CH_3.CHO} + 2HCl$$

(*b*) Chlorination of the methyl group of the acetaldehyde to trichloroacetaldehyde (chloral)—

$$\underset{\text{acetaldehyde}}{CH_3.CHO} + 3Cl_2 \longrightarrow \underset{\text{trichloroacetaldehyde}}{CCl_3.CHO} + 3HCl$$

(*c*) Hydrolysis of trichloroacetaldehyde by the alkali to chloroform and the formate (sodium formate if sodium hypochlorite is used, calcium formate in the case of bleaching powder.)

$$\underset{\text{trichloroacetaldehyde}}{CCl_3.}\boxed{CHO + \underset{\text{from sodium (hypochlorite)}}{NaO}}H \longrightarrow \underset{\text{chloroform}}{CHCl_3} + \underset{\text{sodium formate}}{H.COONa}$$



$$Ca\begin{cases} O\boxed{H \quad CCl_3}CHO \\ \quad + \\ O\boxed{H \quad CCl_3}CHO \end{cases} \longrightarrow 2CHCl_3 + \begin{matrix} HCOO \\ HCOO \end{matrix}\Big\rangle Ca$$

(from bleaching powder) trichloroacetaldehyde chloroform calcium formate

2. *With acetaldehyde.* Reactions (*b*) and (*c*) given above occur.

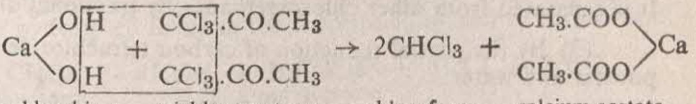
3. *With acetone.*

(*a*) Chlorination of one of the methyl groups in the acetone molecule to give trichloroacetone.

$$\underset{\text{acetone}}{CH_3.CO.CH_3} + 3Cl_2 \longrightarrow \underset{\text{trichloroacetone}}{CCl_3.CO.CH_3} + 3HCl$$

(*b*) Hydrolysis of trichloroacetone by the alkali to chloroform and the acetate.

$$\underset{\text{trichloroacetone}}{CCl_3}\boxed{CO.CH_3 + \underset{\text{(from sodium hypochlorite)}}{NaO}}H \rightarrow \underset{\text{chloroform}}{CHCl_3} + \underset{\text{sodium acetate}}{CH_3.COONa}$$



$$Ca\begin{cases} O\boxed{H \quad CCl_3}.CO.CH_3 \\ \quad + \\ O\boxed{H \quad CCl_3}.CO.CH_3 \end{cases} \rightarrow 2CHCl_3 + \begin{matrix} CH_3.COO \\ CH_3.COO \end{matrix}\Big\rangle Ca$$

(from bleaching powder) trichloroacetone (2 mol) chloroform calcium acetate

Acetone being cheaper than alcohol or acetaldehyde, chloroform is usually prepared from acetone using bleaching powder. The bleaching powder is ground with water in a mortar until a creamy paste is obtained. This is transferred to a flask and the acetone added slowly with shaking. The flask is then fitted with an upright reflux condenser. The reaction usually starts spontaneously after a few minutes, and is so exothermic that it may be necessary to cool the contents by dipping the flask into cold water. When the initial vigorous reaction has subsided the flask is heated on a boiling water bath for a few minutes to complete the reaction. The condenser is then changed to the normal position and the chloroform distilled over. The chloroform collects in the receiver as a dense liquid beneath a layer of water (Fig. 20-2). It is impure containing acetone, water, chlorine, and hydrogen chloride. These impurities are removed by shaking it in turn with a dilute solution of sodium hydroxide and with water. The heavy chloroform layer is then separated and dried over anhydrous calcium chloride. Very pure chloroform may then be obtained by redistillation, the fraction boiling between 60°C and 62°C being collected.

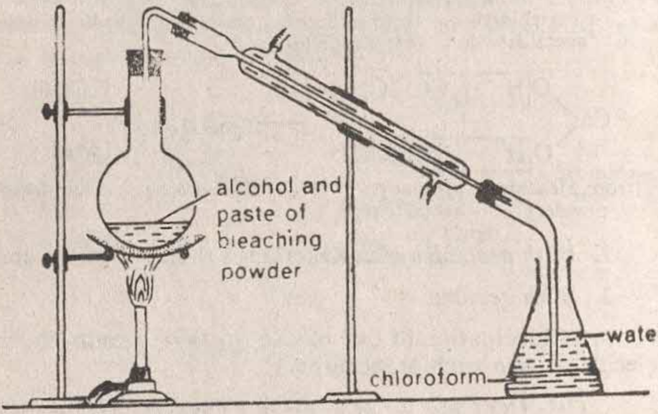


Fig. 20-2. Preparation of chloroform.

**7-2. Manufacture.** (1) *From acetone and bleaching powder* as described under laboratory preparation.

(2) *By the chlorination of methane.* The chlorine is diluted with nitrogen, and the volume ratio of methane, chlorine, and nitrogen is so adjusted that chloroform (trichloromethane) is the main product. It is separated from other chloromethanes by fractional distillation.

(3) By the partial reduction of carbon tetrachloride using iron powder and water.

$$\underset{\text{carbon tetrachloride}}{CCl_4} + 2[H] \xrightarrow{Fe/H_2O} \underset{\text{chloroform}}{CHCl_3} + HCl$$

**7-3. Pure chloroform.** Pure chloroform is best prepared by distilling chloral hydrate with a concentrated aqueous solution of caustic soda or caustic potash.

$$\underset{\text{chloral hydrate}}{CCl_3.\boxed{CH(OH)_2 + NaO}H} \rightarrow \underset{\text{chloroform}}{CHCl_3} + \underset{\text{sodium formate}}{H.COONa} + H_2O$$

## 8. Physical Properties of Chloroform

1. Chloroform is a colourless liquid with a sickly sweetish smell, b.p. 61°C.

2. It has a specific gravity of 1·49 at 15°C.

3. It is almost immiscible with water but readily soluble in alcohol and ether.

4. It is a good solvent for oils, fats, waxes, resins, etc.

## 9. Reactions of Chloroform

1. **Oxidation.** On standing in air, particularly in sunlight, chloroform is oxidized slowly to carbonyl chloride,* a very poisonous gas commonly called phosgene.

$$\underset{\text{chloroform}}{2CHCl_3} + O_2 \xrightarrow{\text{air/sunlight}} \underset{\text{carbonyl chloride}}{2COCl_2} + 2HCl$$

2. **Reduction.** When treated with zinc and water, chloroform is reduced to methane.

$$CHCl_3 + 6[H] \xrightarrow{Zn/H_2O} CH_4 + 3HCl$$

3. **Chlorination.** On chlorination chloroform is converted to carbon tetrachloride, $CCl_4$, the fully substituted chloroderivative of methane.

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

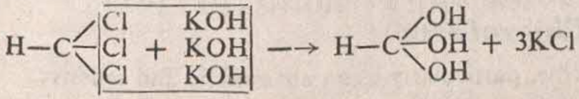
4. **Nitration.** Chloroform reacts with concentrated nitric acid to give nitrochloroform. This compound is a powerful lachrymator and lung irritant, and is commonly known as chloropicrin. It is a liquid which boils at 112°C.

$$\underset{\text{chloroform}}{CHCl_3} + \underset{\text{nitric acid}}{HO.NO_2} \rightarrow \underset{\text{nitrochloroform}}{C(NO_2)Cl_3} + H_2O$$

5. **Hydrolysis.** When chloroform is boiled with an aqueous alkali, it is hydrolysed forming the corresponding salt of formic acid.

$$\underset{\text{chloroform}}{CHCl_3} + 4KOH \rightarrow \underset{\text{pot. formate}}{H.COOK} + 3KCl + 2H_2O$$

Probably the reaction proceeds in two stages. In the first stage the three chlorine atoms in chloroform molecule are replaced by hydroxyl groups.



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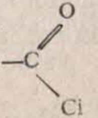
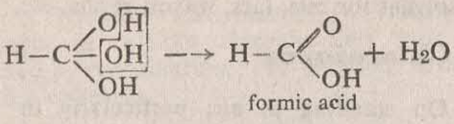
*The structure of carbonyl chloride is 

The resulting compound with three hydroxyl groups attached to one carbon atom is unstable and loses a molecule of water to give formic acid



$$H-C\begin{matrix}\diagup O\boxed{H}\\ -\boxed{OH}\\ \diagdown OH\end{matrix} \longrightarrow \underset{\text{formic acid}}{H-C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown OH\end{matrix}} + H_2O$$

The acid is neutralized by the excess of alkali to give an alkali formate.

$$H.COOH + KOH \rightarrow H.COOK + H_2O$$

**6. Isocyanide reaction.** The most characteristic reaction of chloroform is the formation of an evil-smelling isocyanide when it is warmed with a primary amine, such as aniline, $C_6H_5.NH_2$, and an alcoholic solution of an alkali.

$$\underset{\text{aniline}}{C_6H_5N}\boxed{H_2 + \underset{\text{chloroform}}{Cl_3H}}C + \underset{\text{(alc.)}}{3KOH} \longrightarrow \underset{\text{phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

This reaction is also known as the *carbylamine reaction.* It is used as a test for chloroform (or a primary amine) since the formation of an isocyanide is readily recognized by its nauseating and extremely obnoxious smell.

**7. Formation of acetylene.** When chloroform is heated with silver powder, it is dehalogenated to give acetylene.

$$\underset{\text{chloroform}}{2CHCl_3} + 6Ag \xrightarrow{\Delta} \underset{\text{acetylene}}{CH{\equiv}CH} + 6AgCl$$

## 10. Tests for Chloroform

1. Chloroform has a characteristic sweetish smell.

2. *Isocyanide test.* A little chloroform, contained in a test tube, is gently warmed with a few drops of aniline and alcoholic caustic potash, when an extremely disagreeable smell of phenyl isocyanide is produced.

3. When pure, chloroform does not give a precipitate with silver nitrate solution.

## 11. Uses of Chloroform

1. In medicine, particularly as an anaesthetic and sedative.

2. As an industrial solvent for fats, rubber, alkaloids, iodine, and other substances, and for the extraction of penicillin.

3. For manufacturing tetrafluoroethylene, $F_2C{=}CF_2$, which is polymerized to the plastic $(C_2F_4)_n$ sold under the names 'Teflon' and 'Fluon'.

4. For preserving anatomical specimens.

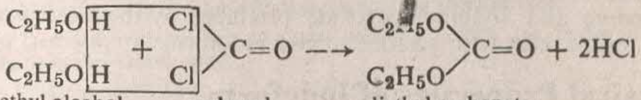
## 12. Chloroform as an Anaesthetic

Inhalation of chloroform vapour causes loss of consciousness (anaethesia). Hence, it is used as a general anaesthetic in surgical operations.* However, the chloroform used as anaesthetic must be very pure and absolutely free from the dangerously poisonous carbonyl chloride which is formed by the action of air and light on chloroform. Following precautions are observed in the storage of chloroform to be used as anaesthetic :

1. It is stored in dark-brown or blue bottles which are kept in a dark place (exclusion of light).

2. The bottles are filled up to the brim and firmly stoppered (exclusion of air).

3. About 2 per cent of ethyl alcohol is added to retard the oxidation of chloroform and convert any carbonyl chloride formed into the relatively harmless diethyl carbonate.



$$\begin{array}{l}C_2H_5O\boxed{H}\\C_2H_5O\boxed{H}\end{array} + \left.\begin{array}{r}\boxed{Cl}\\\boxed{Cl}\end{array}\right\rangle C=O \longrightarrow \left.\begin{array}{l}C_2H_5O\\C_2H_5O\end{array}\right\rangle C=O + 2HCl$$

ethyl alcohol (2 mol.) carbonyl chloride diethyl carbonate

### IODOFORM, $CHI_3$

## 13. Preparation of Iodoform

**13-1. Laboratory preparation.** Chloroform is made by the action of a hypochlorite on ethyl alcohol or acetone. Iodoform, its iodo analogue, is made by the action of a hypoiodite solution on these substances. However, the hypoiodite is unstable, and is made in situ by dissolving iodine in sodium hydroxide solution or sodium carbonate solution, or by using potassium iodide and sodium hypochlorite. The sequence of reactions is the same as in the case of the preparation of chloroform.

(*a*) *With ethyl alcohol.*

$$C_2H_5OH \xrightarrow{O} CH_3.CHO \xrightarrow{I} CI_3.CHO \xrightarrow{NaOH} CHI_3 + H.COONa$$

or, $$\underset{\text{ethyl alcohol}}{C_2H_5OH} + 4I_2 + 6NaOH \rightarrow \underset{\text{iodoform}}{CHI_3} + 5NaI + \underset{\text{sod. formate}}{H.COONa} + 5H_2O$$

(*b*) *With acetone.*

$$CH_3.CO.CH_3 \xrightarrow{I} CI_3.CO.CH_3 \xrightarrow{NaOH} CHI_3 + CH_3.COONa$$

or, $$\underset{\text{acetone}}{CH_3.CO.CH_3} + 3I_2 + 4NaOH \rightarrow \underset{\text{iodoform}}{CHI_3} + 3NaI + \underset{\text{sodium acetate}}{CH_3.COONa} + H_2O$$

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*Other compounds with less serious after-effects are now preferred over chloroform for this purpose.

The reaction may be conveniently carried out in a test tube in two ways :

(*i*) by adding sodium hypochlorite solution to a mixture of acetone (or ethyl alcohol), potassium iodide solution, and sodium hydroxide solution, or

(*ii*) by warming a mixture of acetone (or ethyl alcohol) and sodium hydroxide (or, sodium carbonate solution) to 60°C, and adding iodine in small amounts until a permanent reddish tinge is obtained. A few drops of the alkali solution are then added to discharge the colour.

Crystals of iodoform soon begin to separate as a heavy lemon-yellow solid. These are filtered off, washed thoroughly with water, and recrystallized from methylated spirit.

**13.2. Manufacture**. Iodoform is manufactured by the electrolysis of a hot (10°C) aqueous solution of acetone containing sodium iodide. Iodine and sodium hydroxide produced by the electrolysis of sodium iodide react with acetone to give iodoforn

## 14. Physical Properties of Iodoform

1. Iodoform is a lemon-yellow, crystalline solid, with a strong characteristic smell. It melts at 119°C.

2. It is insoluble in water and is only slightly soluble in alcohol. However, it dissolves freely in warm alcohol, chloroform, and carbon disulphide.

## 15. Reactions of Iodoform

**1. Stability**. Iodoform slowly decomposes in moist air, liberating free iodine. On heating, it decomposes giving off iodine vapour. This explains why iodoform gives a yellow precipitate of silver iodide when heated with silver nitrate solution (chloroform does not give a precipitate of silver chloride).

**2. Reduction.** On reduction with phosphorus and hydriodic acid iodoform gives methylene iodine.

$$\underset{\text{iodoform}}{CHI_3} + 2\,[H] \longrightarrow \underset{\text{methylene iodide}}{CH_2I_2} + 2HI$$

**3. Hydrolysis**. On boiling with alcoholic potash, iodoform undergoes hydrolysis to formic acid which is neutralized by the excess of alkali to give potassium formate The sequence of various steps is the same as in the case of chloroform.

$$\underset{\text{iodoform}}{CHI_3} + 3KOH \rightarrow \underset{\text{formic acid}}{H.COOH} + 3KI + H_2O$$

$$H.COOH + KOH \rightarrow H.COOK + H_2O$$

$$\text{Or,}\quad CHI_3 + 4KOH \rightarrow H.COOK + 3KI + 2H_2O$$

4. **Isocyanide reaction**. When idoform is heated with a primary amine and alcoholic potash, an isocyanide is formed which is readily recognized by its offensive smell.

$$\underset{\text{idoform}}{CHI_3} + \underset{\text{primary amine}}{R.NH_2} + \underset{\text{(alc.)}}{3KOH} \rightarrow \underset{\text{isocyanide}}{R.NC} + 3KI + 3H_2O$$

5. **Formation of acetylene**. When heated with silver powder, iodoform yield acetylene.

$$\underset{\text{iodoform}}{CH}\boxed{I_3 + 6Ag + I_3}\underset{\text{iodoform}}{CH} \rightarrow \underset{\text{acetylene}}{CH{\equiv}CH} + 6AgI$$

## 16. Uses of Iodoform

Iodoform is used as an antiseptic dressing for wounds and ulcers. Its antiseptic action is due to the liberation of free iodine and not due to itself as a substance. Its disagreeable smell is a detriment to its wide use, and it is being replaced by other substances.

### Questions

1. (*a*) List four general methods for preparing alkyl halides.

(*b*) Describe, with the help of a neat, labelled sketch, the preparation of ethyl bromide in the laboratory.

2. What happens when—

(*i*) ethyl chloride reacts with sodium ethoxide,

(*ii*) ethyl bromide is heated with dry silver oxide,

(*iii*) chloroform is heated with aniline and caustic potash,

(*iv*) iodoform is heated with silver powder.

3. How would you prepare from ethyl bromide—

*i*. ethyl alcohol
*ii*. ethyl acetate
*iii*. propylamine
*iv*. butane
*v*. ethane
*vi*. ethylene
*vii*. diethyl ether
*vii*. ethylamine

4. Explain the mechanisms of the substitution reactions of alkyl halides with suitable examples.

5. Discuss the mechanisms of the elimination reactions of alkyl halides corresponding to the $E_2$ reaction and the $E_1$ reaction.

6. (*a*) Give an account of the reactions involved in the preparation of cloroform from ethyl alcohol and from acetone.

(*b*) Describe the manufacture of chloroform from methane.

(*c*) What precautions are taken in storing chloroform for use as an anaesthetic, and why ?

(*d*) What happens when chloroform is treated with zinc and water ? Heated with aqueous alkali ?

7. (*i*) How is iodoform (*a*) prepared in the laboratory and (*b*) manufactured by an electrolytic method ?

(*ii*) Describe the principle reactions of iodoform.

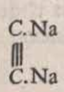
(*iii*) What is the main use of iodoform ?

□ □

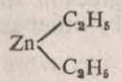
# 21

# Grignard Reagents

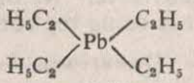
Organic compounds in which a metal atom is directly bonded to carbon are called **organometallic compounds.** Some examples are :



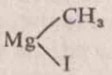
sodium acetylide



diethyl zinc

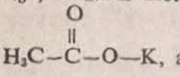


tetraethyl lead



methyl magnesium iodide

Compounds containing metal atoms not directly linked to carbon, *e.g.*, sodium methoxide, $H_3C-O-Na$, and potassium acetate,



$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-O-K$, are not organometallic compounds.

The organometallic compounds of magnesium corresponding to alkylmagnesium halides, RMgX (R=alkyl group, X=a halide), are called Grignard reagents after the name of their French discoverer, Victor Grignard. They are very valuable materials in organic syntheses and can be employed for the preparation of almost all classes of organic compounds.

## 1. Preparation of Grignard Reagents

Grignard reagents are prepared by the action of alkyl halides on magnesium turnings suspended in alcohol-free ether. All the interacting substances and the apparatus used must be dry.

$$\underset{\text{alkyl halide}}{RX} + Mg \xrightarrow{\text{ether}} \underset{\substack{\text{alkyl magnesium halide}\\ \text{(Grignard reagent)}}}{R-Mg-X}$$

$$\underset{\text{methyl iodide}}{CH_3I} + Mg \xrightarrow{\text{ether}} \underset{\text{methyl magnesium iodide}}{CH_3.MgI}$$

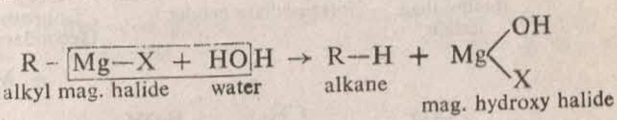
It may sometimes be required to warm the reaction mixture or to add a trace of iodine catalyst to accelerate the reaction. However, when a little Grignard reagent is formed, it catalyses the reaction which proceeds vigorously with evolution of heat. If the reaction tends to become violent, the reaction mixture is cooled externally.

When the reaction is complete, a clear solution of the Grignard reagent in ether is formed.

## 2. Application of Grignard Reagents in Organic Syntheses

Grignard reagents are colourless, non-volatile solids. However, they are not isolated from the ether solution prepared as described above, which is used as such in chemical reactions (ether acts as an inert solvent). Chemically, Grignard reagents are highly reactive. They react with many substances to yield almost all types of organic compounds. The syntheses of a few more important classes of organic compounds from Grignard reagents are outlined in the following paragraphs :

1. **Alkanes.** When the ethereal solution of the Grignard reagent, R–Mg–X, is added to water, a vigorous reaction occurs and a an alkane is formed in a state of high purity.



$$\text{R}-\boxed{\underset{\text{alkyl mag. halide}}{\text{Mg}-\text{X}} + \underset{\text{water}}{\text{HO}}}\text{H} \rightarrow \underset{\text{alkane}}{\text{R}-\text{H}} + \underset{\text{mag. hydroxy halide}}{\text{Mg}\begin{smallmatrix}\text{OH}\\ \text{X}\end{smallmatrix}}$$

$$\underset{\text{methyl mag. iodide}}{CH_3.MgI} + HOH \rightarrow \underset{\text{methane}}{CH_4} + Mg(OH)I$$

$$\underset{\text{ethyl mag. iodide}}{C_2H_5.MgI} + HOH \rightarrow \underset{\text{ethane}}{C_2H_6} + Mg(OH)I$$

Grignard reagents yield alkanes in reactions with alcohols, ammonia, and amines, too.

$$\underset{\text{methyl mag. bromide}}{CH_3\boxed{MgBr} } \hspace{-0.5em}\boxed{+ \underset{\text{ethyl alcohol}}{C_2H_5.O}}H \rightarrow \underset{\text{methane}}{CH_4} + \underset{\text{mag. ethoxy bromide}}{Mg(OC_2H_5)Br}$$

$$\underset{\text{ethyl mag. bromide}}{C_2H_5\boxed{MgBr}}\hspace{-0.5em}\boxed{+ \underset{\text{ammonia}}{NH_2}}H \rightarrow \underset{\text{ethane}}{C_2H_6} + Mg(NH_2)Br$$

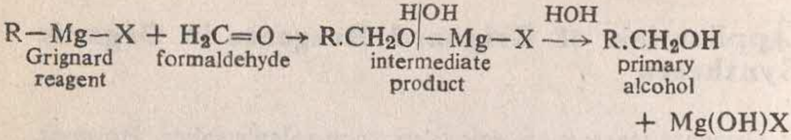
$$\underset{\text{methyl mag. iodide}}{CH_3\boxed{MgI}}\hspace{-0.5em}\boxed{+ \underset{\text{ethylamine}}{C_2H_5.NH}}H \rightarrow \underset{\text{methane}}{CH_4} + Mg(C_2H_5NH)I$$

Higher alkanes can be made from Grignard reagents by reaction with alkyl halides.

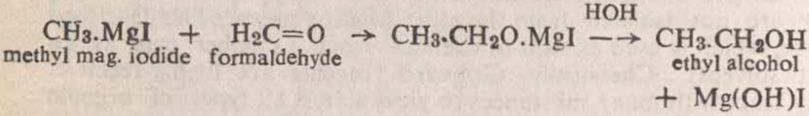
$$\underset{\text{Grignard reagent}}{R-Mg-X} + \underset{\text{alkyl halide}}{X-R'} \rightarrow \underset{\text{alkane}}{R-R'} + \underset{\text{magnesium halide}}{MgX_2}$$

$$\underset{\text{methyl mag. iodide}}{CH_3.MgI} + \underset{\text{ethyl iodide}}{I.C_2H_5} \rightarrow \underset{\text{propane }(C_3H_8)}{CH_3.C_2H_5} + MgI_2$$

2. **Alcohols.** When a Grignard reagent is reacted with formaldehyde and the product hydrolysed, a primary alcohol is obtained.

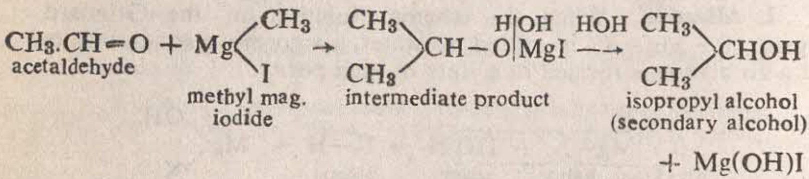


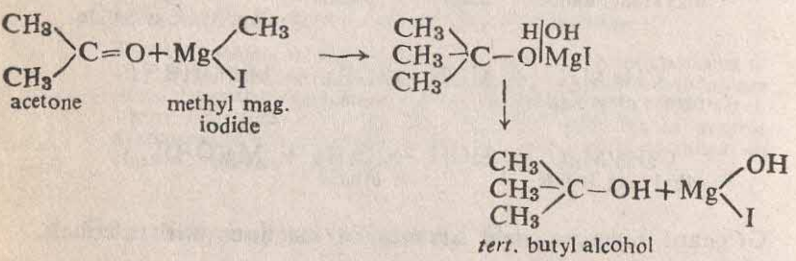
$$\underset{\text{Grignard reagent}}{R-Mg-X} + \underset{\text{formaldehyde}}{H_2C=O} \rightarrow \underset{\text{intermediate product}}{R.CH_2\overset{H|OH}{O|-Mg}-X} \xrightarrow{HOH} \underset{\text{primary alcohol}}{R.CH_2OH} + Mg(OH)X$$



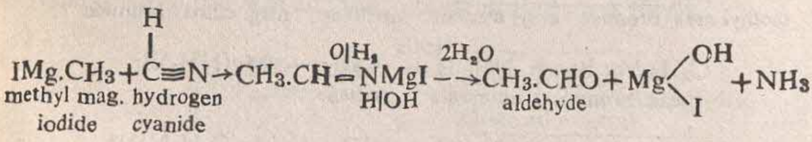
$$\underset{\text{methyl mag. iodide}}{CH_3.MgI} + \underset{\text{formaldehyde}}{H_2C=O} \rightarrow CH_3.CH_2O.MgI \xrightarrow{HOH} \underset{\text{ethyl alcohol}}{CH_3.CH_2OH} + Mg(OH)I$$

If an aldehyde ether than formaldehyde, *e.g.*, $CH_3.CHO$, is used, the product is a secondary alcohol; with ketones, tertiary alcohols are formed.

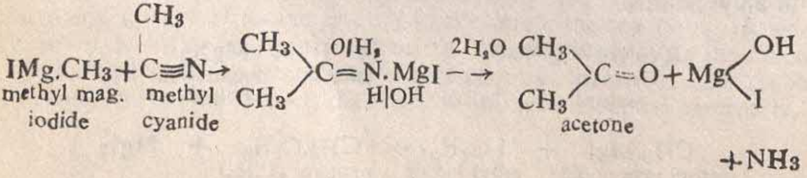

CH₃.CH=O + Mg(CH₃)(I) → (CH₃)₂CH−O(H|OH)MgI —HOH→ (CH₃)₂CHOH + Mg(OH)I
acetaldehyde
methyl mag. iodide
intermediate product
isopropyl alcohol (secondary alcohol)


(CH₃)₂C=O + Mg(CH₃)(I) → (CH₃)₃C−O(H|OH)MgI ↓ (CH₃)₃C−OH + Mg(OH)(I)
acetone
methyl mag. iodide
tert. butyl alcohol

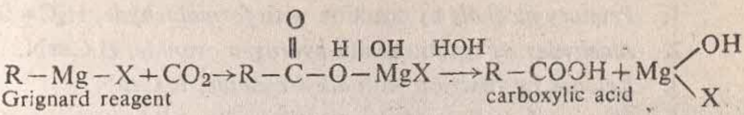
3. **Aldehydes.** These are made from Grignard reagents by reaction with hydrogen cyanide, and hydrolysing the product.


IMg.CH₃ + HC≡N → CH₃.CH=NMgI (O|H₂, H|OH) —2H₂O→ CH₃.CHO + Mg(OH)(I) + NH₃
methyl mag. iodide
hydrogen cyanide
aldehyde

4. **Ketones.** These are formed by adding an alkyl cyanide to the etheral solution of a Grignard reagent, and hydrolysing the addition product with dilute acid.

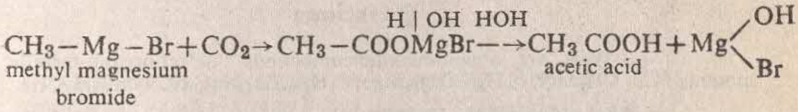

IMg.CH₃ + CH₃C≡N → (CH₃)₂C=N.MgI (O|H₂, H|OH) —2H₂O→ (CH₃)₂C=O + Mg(OH)(I) + NH₃
methyl mag. iodide
methyl cyanide
acetone

5. **Carboxylic acids**. These can be made by adding solid carbon dioxide (dry ice) to a solution of Grignard reagent, and hydrolysing the product with dilute acid.



$$R-Mg-X+CO_2 \rightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-O-MgX \xrightarrow{H\,|\,OH\quad HOH} R-COOH+Mg\begin{matrix}\diagup OH\\ \diagdown X\end{matrix}$$

Grignard reagent carboxylic acid



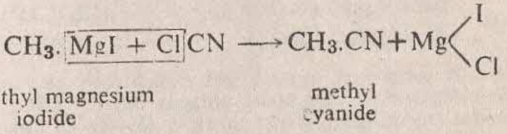
$$CH_3-Mg-Br+CO_2 \rightarrow CH_3-COOMgBr \xrightarrow{H\,|\,OH\quad HOH} CH_3\,COOH+Mg\begin{matrix}\diagup OH\\ \diagdown Br\end{matrix}$$

methyl magnesium bromide acetic acid

This method makes it possible to form an acid from an alcohol of one less carbon atom, e.g., acetic acid (2C) from methyl alcohol (1C).

$$CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow[ether]{Mg} CH_3MgCl \xrightarrow{CO_2} CH_3.COOMgCl \xrightarrow{HOH} CH_3COOH$$

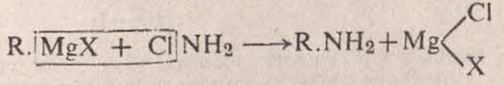
6. **Alkyl cyanides**. Alkyl cyanides are formed by the reaction of Grignard reagent with cyanogen chloride, CNCl. For example,



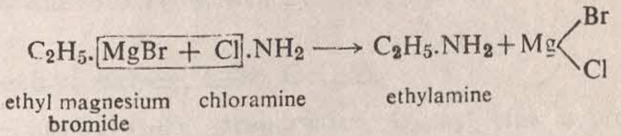
$$CH_3.\boxed{MgI + Cl}CN \longrightarrow CH_3.CN+Mg\begin{matrix}\diagup I\\ \diagdown Cl\end{matrix}$$

methyl magnesium iodide methyl cyanide

7. **Primary amines**. Grignard reagents yield corresponding primary amines with chloramine, $Cl.NH_2$. For example,



$$R.\boxed{MgX + Cl}NH_2 \longrightarrow R.NH_2+Mg\begin{matrix}\diagup Cl\\ \diagdown X\end{matrix}$$



$$C_2H_5.\boxed{MgBr + Cl}.NH_2 \longrightarrow C_2H_5.NH_2+Mg\begin{matrix}\diagup Br\\ \diagdown Cl\end{matrix}$$

ethyl magnesium bromide chloramine ethylamine

**2-1. Review of organic syntheses from Grignard reagents**. Grignard reagents yield the following classes of compounds directly by *double decomposition reactions* with suitable compounds.

1. *Alkanes* by reaction *with water*, alcohols, ammonia, and primary amines
2. *Higher alkanes* by reaction with *alkyl halides*, RX.
3. *Alkyl cyanides* by reaction with *cyanogen chloride*, CNCl.
4. *Primary amines* by reaction with *chloramine*, $ClNH_2$.

The following classes of compounds can be prepared from Grignard reagents by *addition reactions* with suitable compounds, and hydrolysing the products with a dilute acid.

1. *Primary alcohols* by reaction with *formaldehyde*, $H_2C=0$.
2. *Aldehydes* by reaction with *hydrogen eyanide*, $H.C\equiv N$.
3. *Ketones* by reaction with *alkyl cyanide*, $R.C\equiv N$.
4. *Monocarboxylic acids* by reaction with *solid* $CO_2$.

### Questions

1. (*a*) What are organometallic compounds ? Select organo-metallic compounds from $CH_3MgI$, $(CH_3.COO)_2Mg$, $(C_2H_5)_2$ Zn, $NaC\equiv C.Na$, $CH_3ONa$,

(*b*) What are Grignard reagehts ?

(*c*) How are Grignard reagents prepared ?

(*d*) Why is it necessary that the substances and the apparatus used in the preparation of Grignard reagents be dry ?

2. Explain Grignard reagents and their applications in the syntheses of alkanes, primary alcohols, aldehydes, and carboxylic acids.

### Key

1. (*a*) $CH_3.MgI$, $(C_2H_5)_2$ Zn, and $Na.C\equiv C.Na$ are organo-metallic compounds.

(*d*) Because organometallic compounds react with water to yield alkanes.

□ □

# 22

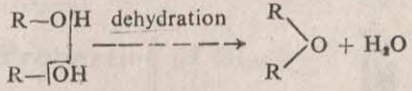
# Ethers

Ethers are compounds of the type R—O—R. That is, an ether consists of two alkyl groups linked directly by an oxygen atom. If the two alkyl groups are identical the ether is called a *simple ether*, *e.g.*, $CH_3.O.CH_3$, $C_2H_5.O.C_2H_5$, etc.; if different, the ether is called a *mixed ether*, *e.g.*, $CH_3.O.C_2H_5$, $CH_3.O.C_3H_7$, etc.

Ethers exhibit isomerism with monohydric alcohols. For instance, dimethyl ether, $CH_3.O.CH_3$, is isomeric with ethyl alcohol, $CH_3.CH_2.OH$, and diethyl ether, $C_2H_5.O.C_2H_5$, is isomeric with butyl alcohol, $C_4H_9OH$. Ethers also exhibit isomerism with members of their own homologous series, a phenomenon called *metamerism*. Thus the following ethers are metamers of the molecular formula $C_4H_{10}O$.

| | |
|---|---|
| $CH_3.CH_2.O.CH_2.CH_3$ | diethyl ether |
| $CH_3O.CH_2.CH_2.CH_3$ | methyl *n*-propyl ether |
| $CH_3.O.CH(CH_3)_2$ | methyl *iso*-propyl ether. |

The ethers may be regarded as the dialkyl derivatives of water (HOH and ROR), as the organic analogues of metallic oxides (Na—O—Na and R—O—R), or as the partial dehydration products of alcohols, thus



$$\begin{matrix} R-O|H \\ R-|OH \end{matrix} \xrightarrow{\text{dehydration}} R_2O + H_2O$$

Diethyl ether is by far the commonest and the most important of the ethers and is often referred to simply as ether.

## 1. Diethyl Ether, $C_2H_5.O.C_2H_5$

**1·1. Laboratory preparation.** Diethyl ether is prepared in the laboratory either from ethyl alcohol or from an ethyl halide.

1. *From alcohol.* When an excess of ethyl alcohol is heated with concentrated sulphuric acid to 140—145°C, the former is partially dehydrated to give diethyl ether.

$$2C_2H_5OH \xrightarrow[140^\circ C]{\text{conc. } H_2SO_4} C_2H_5.O.C_2H_5 + H_2O$$

Probably, the first product of the reaction is ethyl hydrogen sulphate, which then further reacts with the alcohol to form ether.

$$C_2H_5OH + H_2SO_4 \rightarrow C_2H_5.HSO_4 + H_2O$$

$$C_2H_5.HSO_4 + C_2H_5OH \rightarrow C_2H_5.O.C_2H_5 + H_2SO_4$$

Since the sulphuric acid is regenerated, theoretically the same quantity of the acid can be used to convert any amount of alcohol into ether. And, it is for this reason that the method is often described as the '*continuous etherification process*'. In practice, however, side reactions occur causing reduction of some of the sulphuric acid and, in addition, the acid is progressively diluted by the water produced. Hence, if large quantities of alcohol are involved additional small quantities of concentrated sulphuric acid would have to be added periodically.

Concentrated sulphuric acid is added, a little at a time, to the alcohol, with shaking and cooling. The mixture is then heated to 140—145°C in the apparatus shown in Fig. 22-1. Additional alcohol is run in from the tap funnel at about the same rate as the ether distils over. The ether collecting in the receiver contains water, unchanged alcohol, and dissolved sulphur dioxide as impurities. After shaking with sodium hydroxide solution to remove the sulphur dioxide, the upper ether layer is separated and left over anhydrous calcium chloride (which removes both water and alcohol) until it is clear. The liquid is then redistilled; the fraction distilling between 34° to 39°C being pure ether. Very pure ether can be obtained by redistillation over metallic sodium which removes any residual moisture or alcohol.

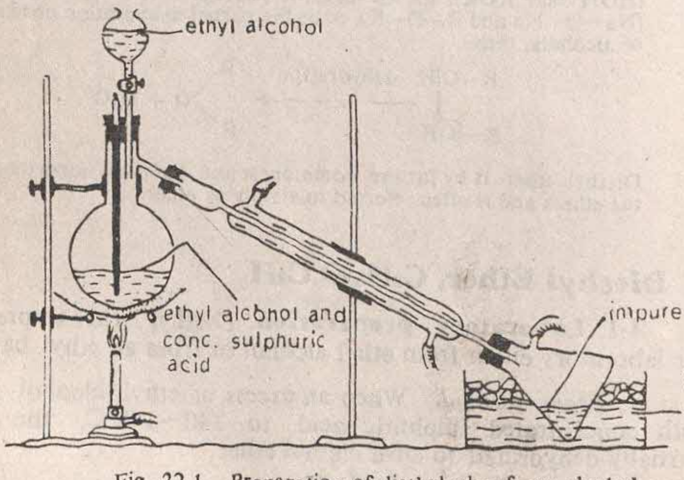


Fig. 22-1. Preparation of diethyl ether from alcohol.

Ether is very volatile and inflammable, and its vapour forms highly explosive mixtures with the air. Hence, it is essential to observe special precautions against fire and explosions when preparing (and using) ether. First, a very efficient condenser and a well-cooled receiver must be used to condense the ether. Secondly, a length of rubber tubing should be attached to the receiver to lead any uncondensed ether vapour to floor level where, being dense, it remains out of reach of flames.

2. *From ethyl halides.* Diethyl ether may be prepared from a ethyl halide, usually ethyl iodide, by either of the following two methods :

(*a*) By heating a mixture of ethyl iodide and sodium ethoxide in alcoholic solution.

$$\underset{\text{ethyl iodide}}{C_2H_5I} + \underset{\text{sodium ethoxide}}{C_2H_5.ONa} \rightarrow \underset{\text{diethyl ether}}{C_2H_5.O.C_2H_5} + NaI$$

This method is known as *Williamson's synthesis.*

(*b*) By warming ethyl iodide with dry silver oxide.

$$2C_2H_5I + Ag_2O \rightarrow C_2H_5.O.C_2H_5 + 2AgI$$

## 2. Manufacture of Diethyl Ether

1. By heating ethyl alcohol (excess) to 140°C with concentrated sulphuric acid, as in the laboratory preparation.

2. By passing ethyl alcohol vapour, at 250°C and under pressure, over a catalyst of alumina. Under these conditions ethyl alcohol is directly dehydrated to diethyl ether.

$$\underset{\text{ethyl alcohol 2 (moles)}}{C_2H_5.O\boxed{H + HO}.C_2H_5} \xrightarrow{Al_2O_3,\ 250^\circ C} \underset{\text{diethyl ether}}{C_2H_5.O.C_2H_5} + H_2O$$

## 3. Physical Properties of Diethyl Ether

1. Diethyl ether is colourless mobile liquid, b.p. 35°C, sp.gr. 0·72, with a characteristic sweet smell.

2. It is miscible with alcohol in all proportions. When mixed with water, some ether dissolves in the water and a little water dissolves in the ether, but this limited solubility can be reduced by the addition of salt.

3. It is a very good solvent for many organic substances.

4. When ether vapour is inhaled it causes unconsciousness, which explains its use as an anaesthetic.

## 4. Reactions of Diethyl Ether

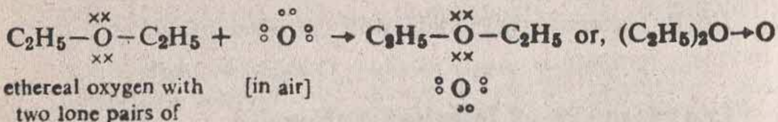
Diethyl ether is very inert chemically, and does not react with metallic sodium, alkalis, cold phosphorus pentachloride, dilute acids, and most of the other common chemical reagents. Its principal reactions may be described as under :

1. **Halogenation**. Diethyl ether gives substitution products with chlorine and bromine. In the dark it reacts with chlorine to give dichloroethyl ether; in the presence of light, perchlorodiethyl ether is formed.

$$\underset{\text{diethyl ether}}{CH_3.CH_2.O.CH_2.CH_3} \xrightarrow[\text{dark}]{Cl_2} \underset{\text{dichlorodiethyl ether}}{CH_3.CHCl.O.CHCl.CH_3}$$

$$\underset{\text{diethyl ether}}{(C_2H_5)_2O} + 5Cl_2 \xrightarrow{\text{light}} \underset{\text{perchlorodiethyl ether}}{(C_2Cl_5)_2O} + 10HCl$$

2. **Oxidation**. Exposed to air for a long time, especially in sunlight, ether slowly forms oxygen forming a peroxide which may explode when heated.



$$C_2H_5-\overset{\times\times}{\underset{\times\times}{O}}-C_2H_5 + \overset{\circ\circ}{\underset{\circ\circ}{:O:}} \rightarrow C_2H_5-\overset{\times\times}{\underset{\underset{\circ\circ}{:O:}}{O}}-C_2H_5 \text{ or, } (C_2H_5)_2O\rightarrow O$$

ethereal oxygen with two lone pairs of electrons

[in air]

diethyl peroxide

This oxidation can be prevented by storing ether in the presence of a little alcohol in dark, well-sealed bottles.

When burnt in air, ether is rapidly oxidized to carbon dioxide and water.

$$C_2H_5.O.C_2H_5 + 6O_2 \rightarrow 4CO_2 + 5H_2O$$

3. **Formation of oxonium salts**. Diethyl ether dissolves in cold, concentrated solutions of mineral acids by forming soluble oxonium salts, *e.g.*, $[(C_2H_5)_2O.H]^+Cl^-$ and $[(C_2H_5)_2O.H]^+HSO_4^-$ with hydrochloric acid and sulphuric acid respectively. Crystalline oxonium salts can be isolated by cooling the solutions to very low temperatures. However, oxonium salts are stable only at low temperatures and in the presence of concentrated acids. If the solution is heated, or diluted with water, a splitting of the ether occurs.

The formation of soluble oxonium salts permits the separation of ether from such organic liquids as ethyl bromide (which do not react with cold acids) by shaking with concentrated hydrochloric or sulphuric acid.

4. **Hydrolysis**. When ether is heated with dilute sulphuric acid under pressure, it hydrolyses to give ethyl alcohol (2 molecules of alcohol for each molecule of ether).

$$\underset{\text{diethyl ether}}{C_2H_5.O.C_2H_5} + \underset{\text{water}}{HOH} \xrightarrow{H_2SO_4} \underset{\text{ethyl alcohol}}{2C_2H_5.OH}$$

5. **With hot concentrated sulphuric acid**. When heated with concentrated sulphuric acid, diethyl ether decomposes to give ethyl hydrogen sulphate.

$$\underset{\text{diethyl ether}}{C_2H_5.O.C_2H_5} + 2H_2SO_4 \longrightarrow \underset{\text{ethyl hydrogen sulphate}}{2C_2H_5.HSO_4} + H_2O$$

6. **With halogen acids**. Dry hydrogen iodide attacks ether even at 0° to give ethyl iodide and ethyl alcohol.

$$\underset{\text{diethyl ether}}{C_2H_5.O.C_2H_5} + HI \xrightarrow{0^\circ} \underset{\text{ethyl iodide}}{C_2H_5I} + \underset{\text{ethyl alcohol}}{C_2H_5OH}$$

At higher temperatures, two molecules of ethyl iodide are formed.

$$C_2H_5.O.C_2H_5 + 2HI \xrightarrow{\Delta} 2C_2H_5I + H_2O$$

Hydrochloric and hydrobromic acids cleave ether much less readily than hydriodic acid; the order of reactivity being

$$HI > HBr > HCl.$$

7. **With phosphorus pentachloride**. Ether does not react with phosphorus pentachloride in cold; on heating it slowly reacts with it to give ethyl chloride.

$$C_2H_5.O.C_2H_5 + PCl_5 \rightarrow 2C_2H_5Cl + POCl_3$$

## 5. Uses of Diethyl Ether

1. *As a solvent*, either for dissolving organic substances or for extracting them from aqueous solutions or suspensions. Many syntheses are carried out in ethereal solutions.

2. *As an anaesthetic* (in conjunction with chloroform and alcohol, or with nitrous oxide and oxygen).

3. *For producing low temperatures*. Very low temperatures may quickly and easily be produced by rapidly evaporating liquid ether. A mixture of ether and solid carbon dioxide is used as a low temperature bath (−110°C) for the liquefaction of gases, etc.

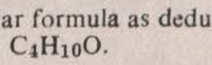
4. *As a composite part of certain medicines*.

## 6. Structure of Diethyl Ether

1. Its molecular formula as deducted from analytical data and molecular weight is $C_4H_{10}O$.

2. That ether neither reacts with sodium to liberate hydrogen nor with phosphorus pentachloride to evolve hydrogen chloride proves the absence of a hydroxyl group in its molecule.

3. Its reaction with hydrogen iodide in cold in which ethyl iodide and ethyl alcohol are formed indicates the presence of two ethyl groups linked through an oxygen atom :



$$C_2H_5-\underset{H}{O}\,\Big|\,\underset{I}{-}C_2H_5$$

4. The above structure for diethyl ether is fully confirmed by its preparation from ethyl iodide and sodium ethoxide.

$$\underset{\text{sodium ethoxide}}{C_2H_5ONa} + \underset{\text{ethyl iodide}}{I.C_2H_5} \rightarrow \underset{\text{diethyl ether}}{C_2H_5-O-C_2H_5} + NaI$$

## 7. Distinction Between Ethyl Alcohol and Diethyl Ether

| *Test* | *Ethyl Alcohol* | *Diethyl Ether* |
|---|---|---|
| 1. Odour | Alcoholic | Ethereal |
| 2. Miscibility with water | Perfectly miscible | Apparently immiscible |
| 3. Action of sodium | Hydrogen liberated | No action |
| 4. Action of $PCl_5$ | Hydrogen chloride evolved in cold | No action in cold |
| 5. With alkali and iodine | Gives Yellow crystals of iodoform | No action |

## Questions

1. (*a*) How is diethyl ether prepared in the laboratory ? Draw a neat, labelled sketch of the apparatus used ?

(*b*) How is diethyl ether manufactured ?

2. (*a*) Describe the main reactions of diethyl ether.

(*b*) List the main uses of diethyl ether.

(c) Give three chemical reactions to differentiate between ethyl alcohol and diethyl ether.

□ □

# 23

# Acid Derivatives

Derivatives of carboxylic acids in which the hydroxyl group of the acid has been replaced are called acid derivatives. The four main classes are *acid chlorides* (also called acyl chlorides), *acid anhydrides*, *acid amides*, and *esters*. These may be regarded as derived from carboxylic acids by the replacement of the OH of the carboxyl by chlorine atom (—Cl), (carboxylate group, R.COO—), amino group ($-NH_2$), and alkoxide group (—OR)

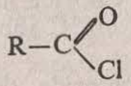
$$R.COOH \rightarrow R.COCl \text{ (acid chloride)}$$
$$R.COOH \rightarrow R.CO.OOC.R \text{ (acid anhydride)}$$
$$R.COOH \rightarrow R.CONH_2 \text{ (acid amide)}$$
$$R.COOH \rightarrow R.COOR \text{ (ester)}$$

As a class, acid chlorides are colourless liquids or solids, have a pungent odour, and are readily hydrolyzed by water. Acid anhydrides, as the name indicates, can also be regarded as derived from acids by dehydration (two molecules of acid losing one molecule of water to yield the acid anhydride). Acid amides are characterized by a weekly amphoteric nature. The esters are usually pleasant smelling compounds. They are primarily responsible for the flavour and fragrance of many flowers and fruits. Ethyl butyrate has the odour of pineapples, *n*-amyl acetate has the odour of bananas, and octyl acetate that of oranges.

In this chapter we shall study one representative member of each of the four classes of acid derivatives, viz., acetyl chloride, acetic anhydride, acetamide, and ethyl acetate, and also some naturally occuring esters.

## 1. Acetyl Chloride, $CH_3.COCl$

This is the most important of the aliphatic acid chlorides, a class of compounds with the general formula $C_nH_{2n+1}.COCl$ and with the structure



Each acid chloride is named by replacing the *-ic* of the acid name by the ending -yl and then adding the term chloride. Thus, the acid chloride derived from butyric acid is named butyryl chloride.

**1-1. Laboratory preparation.** Acetyl chloride can be made by the action of phosphorus trichloride, phosphorus pentachloride, or thionyl chloride on acetic acid or sodium acetate.

$$3CH_3.COOH + PCl_3 \rightarrow 3CH_3.COCl + H_3PO_3$$

$$3CH_3.COONa + PCl_3 \rightarrow 3CH_3.COCl + Na_3PO_3$$

$$CH_3.COOH + PCl_5 \rightarrow CH_3.COCl + POCl_3 + HCl$$

$$CH_3.COOH + SOCl_2 \rightarrow CH_3.COCl + SO_2 + HCl$$

It is usually prepared in the laboratory by the action of phosphorus trichloride on glacial acetic acid. The phosphorus trichloride is slowly added by means of a dropping funnel to glacial acetic acid taken in a round-bottom flask It may be necessary to cool the flask in the earlier stages of the reaction Subsequently, the reaction mixture is heated in a water-bath in the apparatus as shown in Fig. 23-1. The temperature is slowly raised to 45—50°C until the evolution of HCl ceases. The soda-lime tube attached to the receiver serves to trap the hydrogen chloride evolved in the reaction as well as to protect the product from atmospheric moisture. The water-bath is then heated to 100°C when acetyl chloride distills over.

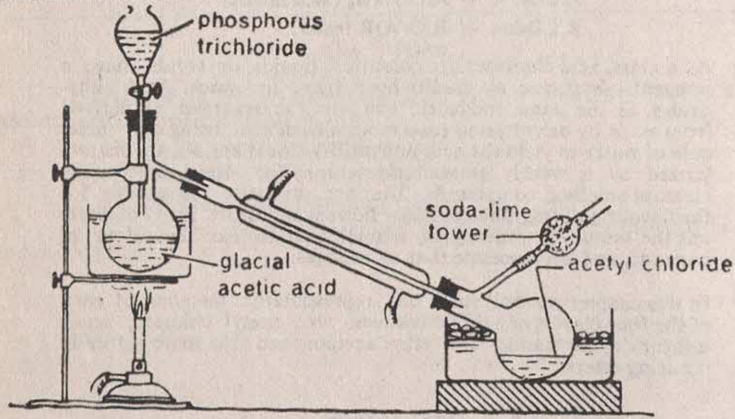


Fig. 23-1. Preparation of acetyl chloride by the action of phosphorus trichloride on acetic acid

**1-2. Physical properties.** Acetic chloride is a colourless, volatile liquid, b p. 52°C, with a pungent smell. The fact that the higher-molecular-weight acetyl chloride has a boiling point of only 52°C, while acetic acid boils at 118°C shows that acetyl chloride is an unassociated compound.

**1-3. Reactions.** Acetyl chloride (like all acid chloride) is characterized by a high order of chemical reactivity. Its important reactions can be described under following headings :

1. *Hydrolysis.* Acetyl chloride reacts with cold water forming acetic acid and giving off hydrogen chloride.

$$CH_3.COCl + H.OH \rightarrow CH_3.COOH + HCl \uparrow$$

It is due to the formation of hydrogen chloride that acetyl chloride fumes strongly in moist air.

The hydrolysis of acetyl chloride with alkalis can be explosive.

2. *Acetylation.* Acetyl chloride will react with any compound having a reactive hydrogen atom (as in –OH and $-NH_2$ groups) and replace it by an acetyl group, $CH_3.CO-$. Such reactions are called acetylation (the term used for acid chlorides, in general, is *acylation*).

i. *With alcohols.* Acetyl chloride reacts vigorously with alcohols at room temperature to give the corresponding acetate esters, *e.g.*, ethyl acetate with ethyl alcohol.

$$\underset{\text{acetyl chloride}}{CH_3.CO}\boxed{Cl + H}\underset{\text{ethyl alcohol}}{O.C_2H_5} \rightarrow \underset{\text{ethyl acetate}}{CH_3.COO.C_2H_5} + HCl\uparrow$$

Similarly, with phenol, $C_6H_5.OH$, it gives phenyl acetate and hydrogen chloride.

$$\underset{\text{acetyl chloride}}{CH_3.COCl} + \underset{\text{phenol}}{HO.C_6H_5} \rightarrow \underset{\text{phenyl acetate}}{CH_3.COO.C_6H_5} + HCl\uparrow$$

In fact, in hydrolysis, too, acetyl chloride replaces one hydrogen atom in water by an acetyl group forming acetic acid.

ii. *With ammonia and amino compounds.* Acetyl chloride reacts with ammonia to form acetamide and with amines ($R.NH_2$) to form substituted amides by replacing one hydrogen atom by the acetyl group, $CH_3.CO-$.

$$\underset{\text{acetyl chloride}}{CH_3.CO}\boxed{Cl + H}\underset{\text{ammonia}}{\text{-}NH_2} \rightarrow \underset{\text{acetamide}}{CH_3.CONH_2} + HCl\uparrow$$

$$\underset{\text{acetyl chloride}}{CH_3.CO}\boxed{Cl + H}\underset{\substack{\text{ethylamine}\\(C_2H_5.NH_2)}}{\text{-}NH.C_2H_5} \rightarrow \underset{\substack{\text{acetyl derivative}\\ \text{of ethylamine}}}{CH_3.CO.NH.C_2H_5} + HCl\uparrow$$

with aniline, $C_6H_5.NH_2$, acetanilide is formed.

$$\underset{\text{aniline}}{C_6H_5\,NH_2} + \underset{\text{acetyl chloride}}{CH_3.COCl} \rightarrow \underset{\text{acetanilide}}{C_6H_5.NH.COCH_3} + HCl\uparrow$$

Acetyl group is often introduced for converting volatile hydroxy compounds or amino compounds into crystalline solids which can be easily purified and identified by their melting points. Acetylation is used as a means to 'protect' amino groups during nitration.

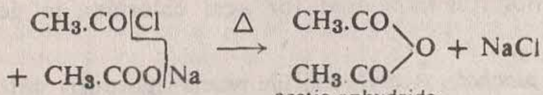
3. *Reduction.* When reduced with hydrogen at 100–150° in the presence of palladium deposited on barium sulphate, acetyl chloride is converted into acetaldehyde (*Rosenmund reaction*).

$$\underset{\text{actyl chloride}}{CH_3.COCl} + H_2 \xrightarrow[100-150^\circ]{Pd/BaSO_4} \underset{\text{acetaldehyde}}{CH_3.\,CHO} + HCl$$

However, reduction of acetyl chloride with lithium aluminium hydride yields ethyl alcohol.

$$\underset{\text{acetyl chloride}}{CH_3.COCl} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{ethyl alcohol}}{CH_3.CH_2OH} + HCl$$

4. *Formation of acetic anhydride.* When acetyl chloride is heated with anhydrous sodium acetate, acetic anhydride is formed.



$$\begin{matrix} CH_3.CO\,Cl \\ + CH_3.COO\,Na \end{matrix} \xrightarrow{\Delta} \begin{matrix} CH_3.CO \\ CH_3.CO \end{matrix}\!\!>\!O + NaCl$$

acetic anhydride

5. *With Grignard reagent.* When acetyl chloride is added to a Grignard reagent, a ketone is formed as the first product. Thus, acetyl chloride reacts with methyl magnesium chloride, $CH_3.MgCl$, to give acetone.

$$\underset{\text{acetyl chloride}}{CH_3.CO}\boxed{Cl + ClMg}\underset{\text{methyl magnesium chloride}}{.CH_3} \longrightarrow \underset{\text{acetone}}{CH_3.CO.CH_3} + MgCl_2$$

6. *With ether.* In the presence of zinc chloride, acetyl chloride reacts with diethyl ether to give ethyl acetate and ethyl chloride.

$$\underset{\text{acetyl chloride}}{CH_3.CO}\boxed{Cl + C_2H_5}\underset{\text{diethyl ether}}{O\,C_2H_5} \rightarrow \underset{\text{ethyl acetate}}{CH_3.COOC_2H_5} + \underset{\text{ethyl chloride}}{C_2H_5Cl}$$

7. *With potassium cyanide.* Acetyl chloride reacts with potassium cyanide in same way as do alkyl halides, giving acetyl cyanide which on hydrolysis forms pyruvic acid.

$$\underset{\text{acetyl chloride}}{CH_3.COCl} \xrightarrow{KCN} \underset{\text{acetyl cyanide}}{CH_3.COCN} \xrightarrow{H_2O} \underset{\text{pyruvic acid}}{CH_3CO.COOH}$$

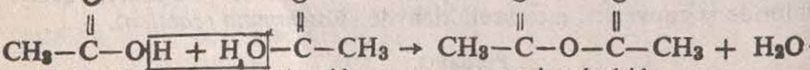
**1-4. Uses.** (1) For the acetylation of alcohols and amines.

(2) For the detection of alcoholic and amino groups in organic compounds.

(3) In organic syntheses.

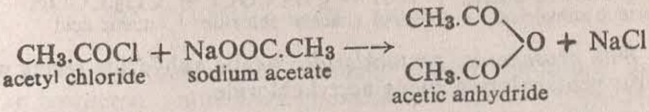
## 2. Acetic Anhydride, $(CH_3.CO)_2O$

This is the most important of the aliphatic acid anhydrides, a class of organic compounds with the general formula $(C_nH_{2n+1}.CO)_2O$. An acid anhydride is formed theoretically by the loss of a molecule of water from two molecules of the acid. The formation of acetic anhydride, for instance, may be shown to take place as follows :



$$\underset{\text{acetic acid}}{CH_3-\overset{\overset{\large O}{\|}}{C}-O}\boxed{H + HO}\underset{\text{acetic acid}}{-\overset{\overset{\large O}{\|}}{C}-CH_3} \rightarrow \underset{\text{acetic anhydride}}{CH_3-\overset{\overset{\large O}{\|}}{C}-O-\overset{\overset{\large O}{\|}}{C}-CH_3} + H_2O$$

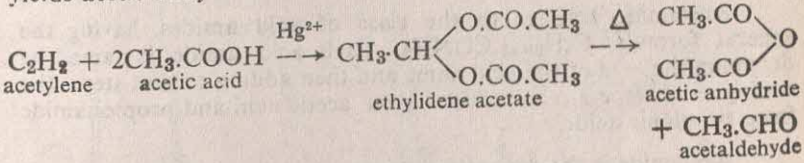
**2-1. Laboratory preparation.** Acetic anhydride is prepared in laboratory by the interaction of acetyl chloride and anhydrous sodium acetate.



$$\underset{\text{acetyl chloride}}{CH_3.COCl} + \underset{\text{sodium acetate}}{NaOOC.CH_3} \longrightarrow \underset{\text{acetic anhydride}}{\begin{matrix} CH_3.CO \\ CH_3.CO \end{matrix}\!\!>O} + NaCl$$

Powdered anhydrous sodium acetate is placed in a flask which is cooled by immersion in cold water and acetyl chloride is added slowly from the dropping funnel. The mixture is gently shaken at intervals. When all the acetyl chloride has been added, the mixture is distilled using an air condenser in place of the usual water condenser. Acetic anhydride distils over between 135-140°C.

**2-2. Manufacture.** Acetyl chloride is manufactured by passing acetylene into glacial acetic acid containing some mercuric sulphate as catalyst. Ethylidene acetate is first formed, which on distillation yields acetic anhydride.



$$\underset{\text{acetylene}}{C_2H_2} + \underset{\text{acetic acid}}{2CH_3.COOH} \xrightarrow{Hg^{2+}} \underset{\text{ethylidene acetate}}{CH_3\text{-}CH\!<\!\begin{matrix} O.CO.CH_3 \\ O.CO.CH_3 \end{matrix}} \xrightarrow{\Delta} \underset{\text{acetic anhydride}}{\begin{matrix} CH_3.CO \\ CH_3.CO \end{matrix}\!\!>O} + \underset{\text{acetaldehyde}}{CH_3.CHO}$$

**2-3. Physical properties.** Acetic anhydride is a colourless liquid, b.p. 139°C,* with a sharp smell similar to that of acetic acid. It is readily soluble in ether and benzene.

**2-4. Reactions.** Acetic anhydride resembles acetyl chloride as an acetylating agent for hydroxy and amino compounds, but is less vigorous in its reactions and therefore more convenient than acetyl chloride.

1. *Hydrolysis.* Acetic anhydride reacts slowly with cold water and rapidly on warming, giving acetic acid.

$$\underset{\text{water}}{HO}\underset{\text{acetic anhydride}}{\boxed{H + CH_3.CO.O}.COCH_3} \rightarrow \underset{\text{acetic acid}}{2CH_3.COOH}$$

2. *Acetylation.* Acetic anhydride reacts with hydroxy and amino compounds forming their acetyl derivatives. In these reactions part of the acetic anhydride molecule is used up in acetylation, and part of the molecule is converted into acetic acid.

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} + \underset{\text{acetic anhydride}}{(CH_3.CO)_2O} \rightarrow \underset{\text{ethyl acetate}}{CH_3.COOC_2H_5} + \underset{\text{acetic acid}}{CH_3.COOH}$$

$$\underset{\text{aniline}}{C_6H_5.NH_2} + \underset{\text{acetic anhydride}}{(CH_3.CO)_2O} \rightarrow \underset{\text{acetanilide}}{C_6H_5.NH.COCH_3} + \underset{\text{acetic acid}}{CH_3.COOH}$$

---

*In general, acid anhydrides have boiling points higher than those of the parent acids.

3. *With dry hydrogen chloride.* Acetic anhydride reacts with dry hydrogen chloride giving acetyl chloride and acetic acid.

$$\underset{\text{acetic anhydride}}{CH_3.CO.O.COCH_3} + \underset{\text{(dry)}}{HCl} \rightarrow \underset{\text{acetyl chloride}}{CH_3.COCl} + \underset{\text{acetic acid}}{CH_3.COOH}$$

4. *With phosphorus pentachloride.* Acetic anhydride reacts with phosphorus pentachloride giving acetyl chloride.

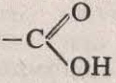
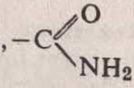
$$\underset{\text{acetic anhydride}}{(CH_3.CO)_2O} + PCl_5 \rightarrow \underset{\text{acetyl chloride}}{2CH_3.COCl} + POCl_3$$

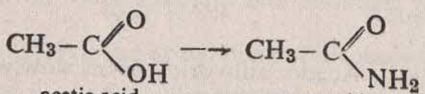
**2-5. Uses.** (1) Mixed with glacial acetic acid, it is used industrially as an acetylating agent in the manufacture of cellulose acetate (acetate rayon), acetanilide, aspirin, and many other acetyl compounds.

(2) For the detection and estimation of hydroxy and amino groups in organic compounds.

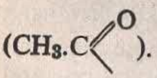
## 3. Acetamide, $CH_3.CONH_2$

Acetamide belongs to the class of acid amides, having the general formula $C_nH_{2n+1}.CONH_2$. Each acid amide is named by dropping the *–ic* of the acid name and then adding to that stem the ending *–amide*, *e.g.*, acetamide from acetic acid and propionamide from propionic acid.

Acetamide is the derivative of acetic acid in which the hydroxyl portion of the carboxyl group,  $-C{\overset{\displaystyle O}{\lt}}_{OH}$ is replaced by the amino ($-NH_2$) group, giving rise to the amide group,  $-C{\overset{\displaystyle O}{\lt}}_{NH_2}$



$$\underset{\text{acetic acid}}{CH_3-C{\overset{\displaystyle O}{\lt}}_{OH}} \longrightarrow \underset{\text{acetamide}}{CH_3-C{\overset{\displaystyle O}{\lt}}_{NH_2}}$$

From another point of view acetamide may be considered as the monoacetyl derivative of ammonia since one of the hydrogen atoms of ammonia ($H.NH_2$) has been replaced by an acetyl group  ($CH_3.C{\overset{\displaystyle O}{\lt}}$).

**3-1. Laboratory preparation.** Acetamide can be prepared by the following reactions.

1. By heating ammonium acetate with excess of glacial acetic acid, when the former is dehydrated to acetamide.

$$\underset{\text{ammonium acetate}}{CH_3.COONH_4} \xrightarrow{\Delta} \underset{\text{acetamide}}{CH_3.CONH_2} + H_2O$$

The acid is used to suppress the dissociation of ammonium acetate into acetic acid and ammonia

$$CH_3.COONH_4 \overset{\Delta}{\rightleftharpoons} CH_3.COOH + NH_3$$

The ammonium acetate is usually prepared in situ by gradually adding powdered ammonium carbonate to excess of glacial acetic acid. The resulting solution of ammonium acetate in acetic acid is then boiled for about an hour using an air condenser (Fig. 23-2 *a*). Ammonium acetate is partially dehydrated to acetamide, and the water vapour escapes through the condenser. The mixture is now transferred to a distilling flask, and the apparatus as shown in Fig. 23-2 (*b*) set up. On heating the flask water and acetic acid distil over first. The fraction distilling between 190° to 210°C is collected and is mainly acetamide which solidifies on cooling. It is purified by recrystallization from acetone.

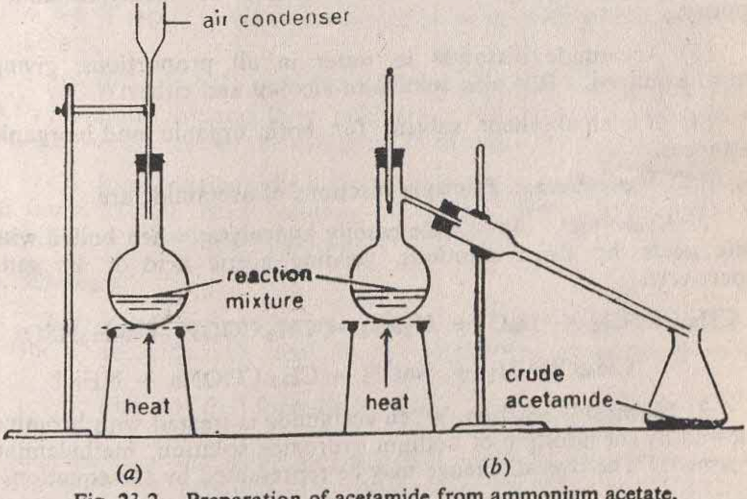


Fig. 23-2. Preparation of acetamide from ammonium acetate.

2. By the action of a concentrated solution of ammonia on acetyl chloride, acetic anhydride, or ethyl acetate.

$$\underset{\text{acetyl chloride}}{CH_3COCl} + 2NH_3 \rightarrow \underset{\text{acetamide}}{CH_3.CONH_2} + NH_4Cl$$

$$\underset{\text{acetic anhydride}}{(CH_3.CO)_2O} + 2NH_3 \rightarrow \underset{\text{acetamide}}{CH_3.CONH_2} + \underset{\text{ammonium acetate}}{CH_3.COONH_4}$$

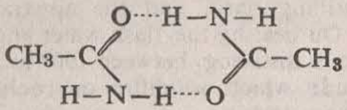
$$\underset{\text{ethyl acetate}}{CH_3.COOC_2H_5} + NH_3 \rightarrow \underset{\text{acetamide}}{CH_3.CONH_2} + \underset{\text{ethyl alcohol}}{C_2H_5OH}$$

The first two of these reactions are convenient and suitable for the laboratory preparation of acetamide.

3. By partial hydrolysis of methyl cyanide with a cold acid (*e.g.*, sulphuric acid) or with alkaline hydrogen peroxide.

$$\underset{\text{methyl cyanide}}{CH_3.CN} + H_2O \xrightarrow[\text{or, conc. } H_2SO_4]{\text{alk. } H_2O_2} \underset{\text{acetamide}}{CH_3.CONH_2}$$

**3-2. Physical Properties.** (1) Acetamide is a colourless crystalline solid, melting at 82°C and boiling at 222°C. Its high boiling point, seemingly incredible for a compound of molecular weight 59, is due to its association by hydrogen bonding into dimeric molecules. The structure of acetamide dimer is



(2) Pure acetamide is odourless, but commercial samples have a characteristic rat-like smell due to traces of methylacetamide impurity.

(3) Acetamide dissolves in water in all proportions, giving neutral solutions. It is also soluble in alcohol and either.

(4) It is an excellent solvent for both organic and inorganic substances.

**3-3. Reactions.** Principle reactions of acetamide are :

*1. Hydrolysis.* Acetamide readily hydrolyses when boiled with dilute acids or alkali solutions, yeilding acetic acid or its salts respectively.

$$CH_3.CONH_2 + H_2O + H_2SO_4 \rightarrow CH_3.COOH + NH_4HSO_4$$

$$CH_3.CONH_2 + NaOH \rightarrow CH_3.COONa + NH_3\uparrow$$

*2. Hofmann's reaction.* When acetamide is treated with bromine followed by the addition of sodium hydroxide solution, methylamine is formed. The overall change may be represented by the equation.

$$\underset{\text{acetamide}}{CH_3.CONH_2}+Br_2+4KOH \rightarrow \underset{\text{methylamine}}{CH_3.NH_2}+2KBr+K_2CO_3+2H_2O$$

It may be noted that the resulting amine has one carbon atom less than acetamide.

*3. With nitrous acid.* Acetamide reacts with nitrous acid (sodium nitrite and dilute hydrochloric acid) giving acetic acid, nitrogen, and water.

$$\underset{\text{acetamide}}{CH_3.CO.}\underbrace{\overbrace{NH_2 + HO.NO}}_{\substack{\text{nitrous acid}\\(HNO_2)}} \rightarrow \underset{\text{acetic acid}}{CH_3.COOH} + H_2O + N_2\uparrow$$

*4. Dehydration.* When distilled with phosphorus pentoxide acetamide is dehydrated to methyl cyanide.

$$\underset{\text{acetamide}}{CH_3.CONH_2} \xrightarrow{P_2O_5} \underset{\text{methyl cyanide}}{CH_3.CN} + H_2O$$

*5. Reduction.* Acetamide is reduced catalytically or by sodium and ethanol to give ethylamine.

$$\underset{\text{acetamide}}{CH_3.CONH_2} + 4[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{ethylamine}}{CH_3.CH_2NH_2} + H_2O$$

*6. Amphoteric character.* Acetamide is very weakly amphoteric. It forms salts such as $CH_3.CONH_2.HCl$, which are unstable and decompose when treated with water. Its weakly acidic character is revealed in the formation of mercury salts when it is boiled with mercuric oxide.

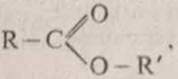
$$2CH_3.CONH_2 + HgO \rightarrow (CH_3.CONH)_2Hg + H_2O$$

**3-4. Tests.** (1) When acetamide is boiled with alkalis, ammonia is liberated.

(2) When it is treated with a solution of sodium nitrite acidified with dilute hydrochloric acid (*i.e.*, nitrous acid), brisk effervescence occurs due to the evolution of nitrogen.

(3) It is distinguished from ammonium acetate by not giving off ammonia with cold solution of caustic soda and by giving no red colour with neutral ferric chloride solution.

## 4 Esters

Esters are organic compounds produced by the interaction of alcohols and acids. Or, they are the derivatives of carboxylic acids corresponding to the formula  $R-C\begin{smallmatrix}\nearrow O \\ \searrow O-R'\end{smallmatrix}$, where R – and R' – groups may be the same or different. Usually, the term ester is restricted to the products of organic acids; the products of inorganic acids being classified in other ways (*e.g.*, as alkyl halides). The reactions between acids and alcohols producing esters are reversible, and are called *esterification.*

ACID + ALCOHOL ⇌ ESTER + WATER (*Esterification*)

Esterification is a very slow reaction, even when heat is applied. It is, therefore, carried out by heating the acid and alcohol in the presence of concentrated sulphuric acid. The latter not only catalyzes the reaction, but also absorbs the water formed, thereby preventing the back-reaction and displacing the equilibrium to the right to a higher yield of the ester.*

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*In case the organic acid reacts with concentrated sulphuric acid, dry hydrogen chloride is bubbled into the reaction mixture of the acid and alcohol. This is known as the *Fischer-Speier* method of esterification.

**4-1. Esters and salts.** Esters are formed by the interaction of acids and alcohols, salts by the interaction of acids and bases; water being essentially formed in both cases. However, the resemblance between esterification and neutralization as also that between esters and salts is only superficial. Neutralization is essentially a reaction between ions and so proceeds almost instantaneously to completion; esterification involves reaction between covalent molecules and is both slow and reversible. The products of these reactions, *viz.*, acids and salts, also differ in several significant respects summarized in the following table.

**Table 23-1.** *Differences between esters and salts*

| *Esters* | *Salts* |
|---|---|
| 1. Esters are mostly volatile, pleasant smelling liquids. | 1. Salts are mostly non-volatile odourless solids. |
| 2. Esters are covalent compounds which do not ionize and are only slightly soluble in water. | 2. Salts are ionic compounds, readily soluble in water and dissociate into ions in solution. |
| 3. All esters show good solubility in a variety of organic solvents. | 3. Salts are usually insoluble in organic solvents. |
| 4. Esters are readily hydrolyzed to give the parent acid and alcohols. | 4. Except the salts of weak acids or weak bases, the salts do not hydrolyse. |
| 5. Esters are neutral in character. | 5. In solution, salts may be neutral, or acidic or basic due to hydrolysis. |

**4-2. Nomenclature.** Despite the structural differences between esters and salts, esters are given names which resemble those used for the salts of the corresponding acid :

| $CH_3.COONa$ | $CH_3.COOC_2H_5$ |
|---|---|
| sodium acetate | ethyl acetate |

The base of the name refers to the part of the structure related to the acid, *formate*, *acetate*, *propionate*, etc. It is preceded by the name of the alkyl radical in the alcohol involved in the preparation of the ester, *methyl*, *ethyl*, *propyl*, etc.

**4-3. Importance of esters.** Esters are an important class of organic compounds not only for their numerous applications in industry, but also because they include such biologically important substances as fats. They are distributed widely in nature and contribute to the characteristic fragrance of flowers and the flavours of fruits. In industry they are employed as perfume and flavouring materials, solvents, synthetic agents, and for the preparation of plastics. For the production of commercial perfumes and flavours numerous organic esters are made by synthetic methods and are used either alone or blended with natural products. Naturally occurring esters of glycerol and higher fatty acids, *viz.*, fats and oil are used for the manufacture of soaps and glycerol, and in foods.

**4-4. Identification of esters.** Esters are identified by recognizing the products of their hydrolysis. The given ester is boiled under reflux with an alkali for about 30 minutes, when it is hydrolysed into an alcohol and the salt of an acid. The alcohol is distilled off, collected, and recognized by the usual tests. The non-volatile salt left behind in the distillation flask is acidified for liberating the acid which is isolated by distillation (or by filtration, if insoluble), and recognized by applying the usual tests. Ethyl acetate treated in this way, for example, would yield ethyl alcohol in the first distillate, and acetic acid in the second. With the identification of these products, the identity of the ester is at once deduced.

## 5. Ethyl Acetate, $CH_3.COOC_2H_5$

Ethyl acetate is much the most well-known of esters, and in many respects typical of this class of organic compounds.

**5-1. Laboratory preparation.** Ethyl acetate can be prepared by the following reactions :

1. By the interaction of acetyl chloride or acetic anhydride with ethyl alcohol.

$$\underset{\text{acetyl chloride}}{CH_3.CO\boxed{Cl\ +\ H}}\underset{\text{ethyl alcohol}}{O.C_2H_5} \rightarrow \underset{\text{ethyl acetate}}{CH_3.COO.C_2H_5} + HCl$$

$$\underset{\text{acetic anhydride}}{(CH_3.CO)_2O} + \underset{\text{ethyl alcohol}}{C_2H_5OH} \rightarrow \underset{\text{ethyl acetate}}{CH_3.COO.C_2H_5} + \underset{\text{acetic acid}}{CH_3.COOH}$$

2. By heating ethyl iodide with silver acetate, and filtering off the insoluble silver iodide after the reaction is over.

$$\underset{\text{silver acetate}}{CH_3.COO\boxed{Ag\ +\ I}}\underset{\text{ethyl iodide}}{.C_2H_5} \xrightarrow{\Delta} \underset{\text{ethyl acetate}}{CH_3.COO.C_2H_5} + AgI$$

3. By heating ethyl alcohol with glacial acetic acid to 140°C in the presence of concentrated sulphuric acid.

$$\underset{\text{acetic acid}}{CH_3.CO\boxed{OH\ +\ H}}\underset{\text{ethyl alcohol}}{O.C_2H_5} \rightleftharpoons \underset{\text{ethyl acetate}}{CH_3.COO.C_2H_5} + \underset{\text{water}}{H_2O}^{*}$$

---

*The older view that esterification involved the hydrogen of the carboxyl group of the acid and the hydroxyl of the alcohol as shown in the equation.

$$CH_3.COO\boxed{H\ +\ HO}.C_2H_5 \rightleftharpoons CH_3.COO.C_2H_5 + H_2O$$

was experimentally proved to be incorrect by Roberts and Urey in 1938, who used labelled oxygen atoms $^{18}O$ in the acid and the alcohol to study the reaction mechanism. They found that the oxygen in the water formed came from the acid and not from the alcohol.

This is the most usual method for the preparation of ethyl acetate in laboratory. A mixture of equal volumes of ethyl alcohol and concentrated sulphuric acid is prepared by adding the acid in a slow stream to the alcohol with shaking. The apparatus is then set up as shown in Fig. 23-3, and the acid-alcohol mixture heated on an oil-bath to about 150°C. A mixture of equal volumes of ethyl alcohol and glacial acetic acid is added from a tap funnel at about the same rate at which the ethyl acetate distils over into the receiver. The product is impure containing alcohol, acetic acid, ether, and sulphurous acid. It is shaken with a saturated solution of sodium carbonate in a separating funnel to remove the acidic impurities. The upper layer is separated, and shaken with a concentrated solution of calcium chloride to remove ethyl alcohol. The upper ethyl acetate layer is again separated and dried by leaving it to stand over lumps of anhydrous calcium chloride until the liquid is clear. It is then filtered and carefully distilled on a water bath, the fraction boiling between 74°C to 79°C being ethyl acetate almost free of ether.

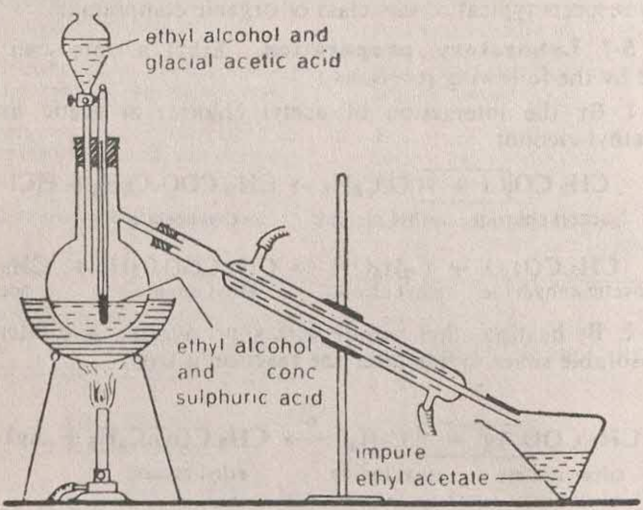


Fig. 23-3. Preparation of ethyl acetate from ethyl alcohol and acetic acid.

**5-2. Physical properties.** (1) Ethyl acetate is a colourless liquid with a pleasant fruity smell, sp. gr. 0·90.

(2) It boils at 77°C, the comparatively low boiling point (its isomeric *n*-butyric acid, $C_3H_7.COOH$, boils at 164°C) indicating the non-associated character of ethyl acetate.

(3) Ethyl acetate is only slightly soluble in water but dissolves readily in organic solvents such as alcohol and ether.

5-3. **Reactions**. The important reactions of ethyl acetate are :

*1. Hydrolysis.* When hydrolysed, ethyl acetate yields ethyl alcohol and acetic acid. With water alone the hydrolysis occurs extremely slowly, even on boiling.

$$\underset{\text{ethyl acetate}}{CH_3.COO.C_2H_5} + \underset{\text{water}}{H.OH} \rightleftharpoons \underset{\text{acetic acid}}{CH_3.COOH} + \underset{\text{ethyl alcohol}}{C_2H_5OH}$$

The hydrolysis is catalysed both by hydrogen ions from mineral acids and by hydroxyl ions from alkalis, the rate of reaction being proportional to the concentration of these ions. However, the hydrolysis occurs most rapidly with the alkalis, and particularly so with alcoholic solutions of the latter. In the alkaline hydrolysis, sodium (or potassium acetate) and ethyl alcohol are formed.

$$\underset{\text{ethyl acetate}}{CH_3.COO.C_2H_5} + NaOH \rightarrow \underset{\text{sodium acetate}}{CH_3.COONa} + \underset{\text{ethyl alcohol}}{C_2H_5OH}$$

Alkaline hydrolysis of fats and oils, the glyceride esters of higher fatty acids, is conducted on a large scale in the manufacture of soaps which are the alkali salts of the higher fatty acids. Because of this association with the production of soaps, alkaline hydrolysis is also known as **saponification.**

2. *With ammonia.* When ethyl acetate is shaken with a concentrated solution of ammonia, acetamide and ethyl alcohol are formed.

$$\underset{\text{ethyl acetate}}{CH_3.COO.C_2H_5} + \underset{\text{ammonia}}{NH_3} \rightarrow \underset{\text{acetamide}}{CH_3.CONH_2} + \underset{\text{ethyl alcohol}}{C_2H_5OH}$$

This reaction is called *ammonolysis, i.e.* "splitting by ammonia".

3. *Reduction.* When reduced by lithium aluminium hydride, $LiAlH_4$, by an alcohol and metallic sodium, or by hydrogen at high pressures, ethyl acetate gives ethyl alcohol.

$$CH_3.COO.C_2H_5 + 4[H] \rightarrow 2C_2H_5OH$$

4. *With phosphorus pentachloride.* Ethyl acetate reacts with phosphorus pentachloride to give acetyl chloride and ethyl chloride.

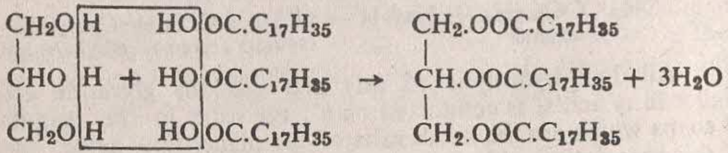
$$\underset{\text{ethyl acetate}}{CH_3.COO.C_2H_5} + PCl_5 \rightarrow \underset{\text{acetyl chloride}}{CH_3.COCl} + \underset{\text{ethyl chloride}}{C_2H_5Cl} + POCl_3$$

5-4. **Uses**. Ethyl acetate is chiefly used as a solvent for cellulose nitrate in quick-drying lacquers and in nail polishes.

## 6. Fats and Oils

All fats and oils of vegetable or animal origin are complex mixtures of the esters of glycerol, known as *glycerides.* The aliphatic acids esterified with glycerol in the natural fats contain an even number of carbon atoms varying from 4 to 26, but the majority of the acids contain 16 or 18 carbon atoms. Ordinarily, the acids are of the straight-chain variety, and these may be saturated (*e.g.*, stearic acid, $C_{17}H_{35}.COOH$) or unsaturated (*e.g.*, oleic acid, ($C_{17}H_{33}.COOH$). Chemically, there is not much significant difference between fats and oils. The glycerides of saturated acids of high molecular weight, being solids at room temperature, are called *fats*. The glycerides of acids of low molecular weight or of highly unsaturated acids, being liquids at ordinary temperature, are called *oils*. **Butter fat** differs from all the other fats in containing glycerides of lower acids, mainly butyric acid ($C_3H_7.COOH$), caproic acid ($C_5H_{11}.COOH$), caprylic acid ($C_7H_{15}.COOH$), and capric acid ($C_9H_{19}.COOH$).

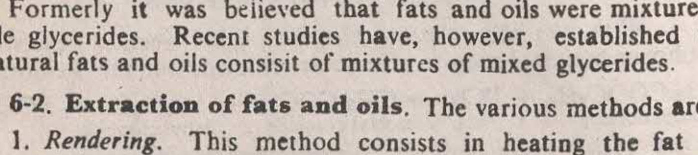
**6-1. Types of glycerides.** Glycerides are of two broad types : simple and mixed. In *simple glycerides* the three hydroxyl groups of glycerol are esterified with three molecules of the same acid. Glyceryl tristearate (called, stearin), illustrated below, is an example of a simple glyceride :



$$\begin{array}{lcl} CH_2O\,H \quad HO\,OC.C_{17}H_{35} & & CH_2.OOC.C_{17}H_{35} \\ | & & | \\ CHO\,H + HO\,OC.C_{17}H_{35} & \rightarrow & CH.OOC.C_{17}H_{35} + 3H_2O \\ | & & | \\ CH_2O\,H \quad HO\,OC.C_{17}H_{35} & & CH_2.OOC.C_{17}H_{35} \end{array}$$

glycerol stearic acid glyceryl tristearate

In *mixed glycerides* each molecule of glycerol has been esterified with two or even three different acids. Glycerol palmito-stearo-oleate derived from palmitic acid ($C_{15}H_{31}.COOH$), stearic acid ($C_7H_{35}.COOH$), and oleic acid ($C_{17}H_{33}.COOH$) is an example of a mixed glyceride.



$$\begin{array}{lcl} CH_2O\,H \quad HO\,OC.C_{15}H_{31} & & CH_2.OOC.C_{15}H_{31} \\ | & & | \\ CHO\,H + HO\,OC.C_{17}H_{35} & \rightarrow & CH.OOC.C_{17}H_{35} + 3H_2O \\ | & & | \\ CH_2O\,H \quad HO\,OC.C_{17}H_{33} & & CH_2.OOC.C_{17}H_{33} \end{array}$$

glycerol palmito-stearo-oleate

Formerly it was believed that fats and oils were mixtures of simple glycerides. Recent studies have, however, established that all natural fats and oils consisit of mixtures of mixed glycerides.

**6-2. Extraction of fats and oils.** The various methods are :

1. *Rendering.* This method consists in heating the fat and oils containing animal tissue with water or steam, when the fat rises to the surface and is skimmed off. Tallow is made in this way from mutton and lard from pig-meat.

2. *Pressing.* Most vegetable oils are obtained by crushing the fruits or seeds of the plant between rollers and then pressing in a hydraulic press so that the oil is squeezed out. The principal sources are peanuts, coconuts, cottonseed, castor beans, palms, linseed, soya beans, and olives. The pressed cake is used as fodder for milch cattle.

3. *Solvent extraction.* The pressing method does not remove the oil completely, and small amounts are left in the pressed cake.

These are often recovered by extraction with a solvent such as benzene, petroleum ether, or carbon disulphide.

After extraction by any of the above methods, the crude oil is treated with a little alkali to remove any free acids as also the colloidal impurities. The oil is then decolorized by agitation with plaster of Paris and animal charcoal at 70°-80°C, and then deodorized with steam.

**6-3. Physical properties.** 1. At ordinary temperature, oils are liquids, while fats are solids, with no odour or taste in the pure state.

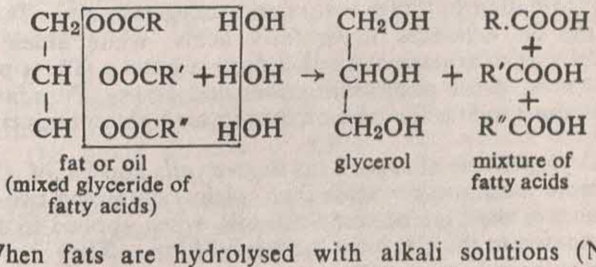
2. They are lighter than water, and immiscible with it; therefore, when mixed with water they separate in the upper layer.

3. They dissolve freely in organic solvents such as chloroform, carbon tetrachloride, ether, acetone, and benzene.

4. They can be emulsified with water in the presence of soap, gelatine, or any other emulsifier.

**6-4. Reactions.** The chemical reactions of fats and oils are, in fact, the reactions of the glycerides of the saturated and unsaturated fatty acids they consist of. They main reactions are :

1. *Hydrolysis.* When fats are heated with water or dilute acids under pressure, they are hydrolysed to give glycerol and free fatty acids.

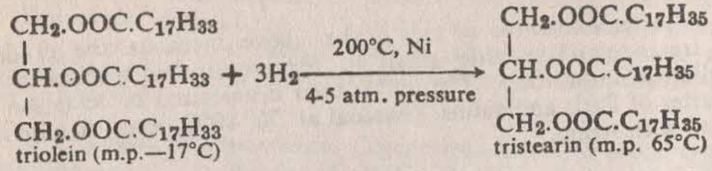


$$\begin{array}{lllcllcl} CH_2 & \boxed{OOCR} & H\,OH & & CH_2OH & & R.COOH \\ | & & & & | & & + \\ CH & OOCR' & +H\,OH & \rightarrow & CHOH & + & R'COOH \\ | & & & & | & & + \\ CH & OOCR'' & H\,OH & & CH_2OH & & R''COOH \end{array}$$

When fats are hydrolysed with alkali solutions (NaOH or KOH), the products are glycerol and the alkali salts of fatty acids (*e.g.*, sodium stearate, sodium palmitate, etc.), called soaps.

2. *Hydrogenation.* When a vegetable oil is heated with hydrogen under 2-5 atmospheres pressure at about 200°C in the presence of a catalyst of finely divided nickel, the unsaturated acid radicals take up the hydrogen by addition across their double bonds and change into corresponding saturated acid radicals. The melting point of the oil is raised by this change; *i.e.*, an oil is converted into a fat. Thus, the glyceride of the unsaturated oleic acid, triolein,

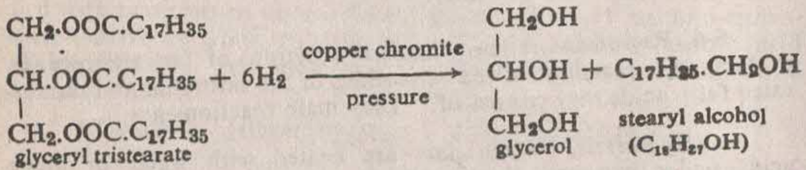
m.p.—17°C, is hydrogenated to the glyceride of the saturated stearic acid, tristearin, m.p. 65°C.



$$\begin{array}{l} CH_2.OOC.C_{17}H_{33} \\ | \\ CH.OOC.C_{17}H_{33} \\ | \\ CH_2.OOC.C_{17}H_{33} \\ \text{triolein (m.p.—17°C)} \end{array} + 3H_2 \xrightarrow[\text{4-5 atm. pressure}]{\text{200°C, Ni}} \begin{array}{l} CH_2.OOC.C_{17}H_{35} \\ | \\ CH.OOC.C_{17}H_{35} \\ | \\ CH_2.OOC.C_{17}H_{35} \\ \text{tristearin (m.p. 65°C)} \end{array}$$

The hydrogenation of oils is carried out on a large scale for the production of fats since the latter are more acceptable than oils for cooking and eating and also for soap making. The extent of hydrogenation is carefully controlled so that the partially hydrogenated fat at room temperature is about as soft a solid as lard. Fully saturated fats are all too hard to be useful as kitchen shortenings.

3. *Hydrogenolysis* (*complete reduction*). If hydrogenation of an oil or a fat is carried in the presence of a catalyst of copper, the ester linkages in the glycerides are splitted. This produces glycerol, and long-chain alcohols by the reduction of the fatty acids. For instance, glyceryl tristearate yields glycerol and stearyl alcohol.



$$\begin{array}{l} CH_2.OOC.C_{17}H_{35} \\ | \\ CH.OOC.C_{17}H_{35} \\ | \\ CH_2.OOC.C_{17}H_{35} \\ \text{glyceryl tristearate} \end{array} + 6H_2 \xrightarrow[\text{pressure}]{\text{copper chromite}} \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{glycerol} \end{array} + \begin{array}{c} C_{17}H_{35}.CH_2OH \\ \text{stearyl alcohol} \\ (C_{18}H_{37}OH) \end{array}$$

4. *Rancidification*. Fats and oils tend to spoil on storage and become rancid. Rancidification of fats involves their hydrolysis and oxidation by the moisture and oxygen in air. The hydrolysis of the fat produces lower fatty acids while aldehydes are produced by the oxidation at the double bond. These products, even in traces, cause unpleasant odour and taste. Pure fats can be stored without spoiling for long periods in air-tight containers.

5. *Drying*. Some oils, such as *linseed oil*, consist of the esters of still more unsaturated acids than oleic, containing two or three double bonds in their molecules.* Such oils, when applied to a surface and left exposed to the air, form hard solid films. They are known as *drying oils* and are used for the preparation of oil paints and varnishes. The change that occurs in the drying oils is believed to involve oxidation and polymerization at the double bonds in the unsaturated acid radicals. To make them dry more rapidly the oils are boiled in the presence of oxides of cobalt, manganese, or lead, which catalyze the chemical changes involved in the formation of the film.

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* Examples of such acids are linoleic acid, $C_{17}H_{31}.COOH$, and linolenic acid, $C_{17}H_{29}.COOH$. Linseed oil is mainly composed of the glycerides of these two acids.

**6-5. Uses.** (1) *In human diet.* The combustion of 1 gram of fat produces about 9500 calories against 4400 calories from 1 gram of protein and 3961 calories from 1 gram of cane sugar. Hence, the fats are the richest source of energy in foods, and account for up to half of the energy content of the human diet. Excess fats are stored in the body to be oxidized as needed at some future time.

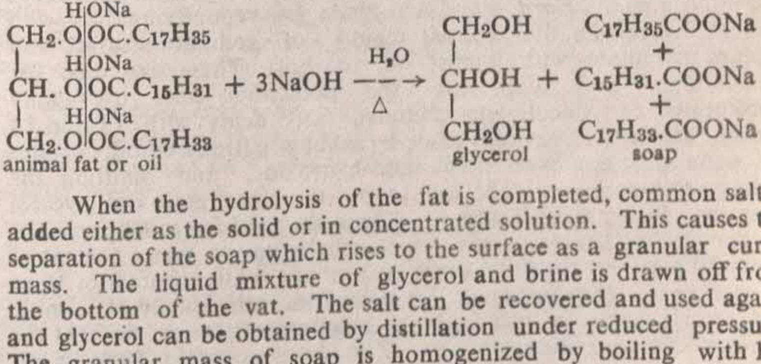
(2) *In making soaps* of all kinds, fatty acids, and glycerol.

(3) *In the manufactures of certain explosives and plastics.*

(4) As such in *paints, varnishes, lubricants, cosmetics, etc.*

## 7. Soaps

When fats and oils are boiled with aqueous sodium hydroxide, they are hydrolyzed or 'saponified' to give glycerol and the sodium salts of the acids contained in their glycerides. The sodium salts of higher fatty acids containing from 10 upward to as many as 26 carbon atoms are called *soaps.* Since natural fats and oils are mixtures of mixed glycerides, their hydrolysis produces a mixture of sodium salts of various acids. However, most samples of soap have the largest percentage of three salts, viz., sodium stearate ($C_{17}H_{35}.COONa$), sodium palmitate ($C_{15}H_{31}.COONa$), and sodium oleate ($C_{17}H_{33}.COOH$). Hence, soaps are usually, represented by the formulas of these salts.



$$\begin{array}{l} \quad\;\; H|ONa \\ CH_2.O|OC.C_{17}H_{35} \\ | \quad\; H|ONa \\ CH.\,O|OC.C_{15}H_{31} \\ | \quad\; H|ONa \\ CH_2.O|OC.C_{17}H_{33} \\ \text{animal fat or oil} \end{array} + 3NaOH \xrightarrow[\Delta]{H_2O} \begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{glycerol} \end{array} + \begin{array}{c} C_{17}H_{35}COONa \\ + \\ C_{15}H_{31}.COONa \\ + \\ C_{17}H_{33}.COONa \\ \text{soap} \end{array}$$

When the hydrolysis of the fat is completed, common salt is added either as the solid or in concentrated solution. This causes the separation of the soap which rises to the surface as a granular curdy mass. The liquid mixture of glycerol and brine is drawn off from the bottom of the vat. The salt can be recovered and used again, and glycerol can be obtained by distillation under reduced pressure. The granular mass of soap is homogenized by boiling with hot water or by blowing in steam, run off into wooden moulds, and allowed to solidify. In the manufacture of toilet soaps, perfume and colouring matter is added before homogenizing the soap curds.

In modern *continuous process* for soap-making, the fats are hydrolyzed into glycerol and free fatty acids, and the latter converted into soaps by treatment with alkali, or used for other purposes. In one process, the fat is heated with water at high temperatures and pressure in the presence of small amounts of lime or zinc oxide. In another process, the fat is heated with water at 100°C in the presence of about 1 per cent of naphthalene sulphuric acid (Twitchell reagent) which catalyzes the hydrolysis of glycerides. The fatty acids produced by these methods rise to the surface and are continuously drawn out, while the fat is fed in at the same rate as shown in Fig. 23-4. Glycerol mixed with water is continuously drawn off from the bottom. The fatty acids are pumped to another vessel where they are converted into soaps by treatment with sodium hydroxide or sodium carbonate solution.

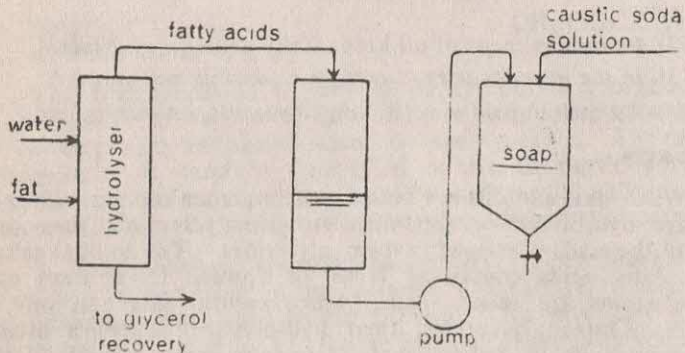


Fig. 23-4. Continuous process for soap-making.

**7-1. Kinds of soap.** Two main kinds of soaps are : hard soaps and soft soaps. *Hard soaps* are made by saponifying fats with sodium hydroxide, and consist mainly of sodium stearate and sodium palmitate with almost no alcohol. These are used for laundering. Soft soaps are the potassium salts of mainly unsaturated fatty acids, or saturated fatty acids with 12 and 14 carbon atoms. These are made by boiling cottonseed oil, coconut oil, palm oil, etc. with potassium hydroxide, and omitting the salting-out operation. The soft soaps, therefore retain the glycerol liberated during saponification. These are used for toilet purposes. In contrast to laundry soaps which usually have a water content of about 30 per cent, the toilet soaps have a low water content of 10 to 15 per cent. *Shaving soaps* are potassium salts chiefly of palmitic and stearic acids, with additional amounts of glycerol (so that the lather would not rapidly dry up). *Liquid soaps* contain 70 to 85 per cent water, and are made by the saponification of coconut oil with potassium hydroxide. *Floating* soaps are made by beating tiny air bubbles into the soaps to make them less dense than water. Special additives are sometimes introduced into soap. Thus *carbolic soap*, which has a disinfectant action, contains about 0·5 per cent of phenol, *tar soap*, upto 5 per cent of birch tar, etc.

**7-2. Cleansing action of soap.** Soap cleanses by emulsifying grease which holds the dirt to the fabric, thus loosening the dirt. The dislodged dirt is then absorbed on the colloidal particles of soaps, and carried away by the froth.

## 8. Waxes

The animal and vegetable waxes are esters of *higher fatty acids* and *long-chain monohydric alcohols*, of the general formula R.COOR′. The hydrolysis of a wax gives an acid and an alcohol, each containing 16 to 31 carbon atoms. Often the natural wax contains, in addition to the ester, small amounts of the long-chain free acid and the long-chain alcohol. The acids and alcohols which occur most frequently in waxes include the following :

| | | | |
|---|---|---|---|
| Palmitic acid, | $C_{15}H_{31}.COOH$ | Cetyl alcohol. | $H_{16}H_{33}OH$ |
| Cerotic acid, | $C_{25}H_{51}.COOH$ | Ceryl alcohol, | $C_{26}H_{53}OH$ |
| Melissic acid, | $C_{30}H_{61}.COOH$ | Myricyl alcohol, | $C_{31}H_{63}OH$ |

Like the fats and oils, waxes also yield soaps upon alkaline hydrolysis; the other product, however, is a high molecular-weight alcohol and not glycerol.

**8-1. Beeswax.** Beeswax consists largely of myricyl palmitate $C_{15}H_{31}.COO.C_{31}H_{63}$, and free cerotic acid. It is obtained from the honeycomb of the bee. The natural product, which is yellow, is bleached to the white wax for use in the manufacture of furniture, floor, and car polishes, in cosmetics, in lithographic inks, in waterproofing, and in certain pharmaceutical preparations.

**8-2. Carnauba wax.** Carnauba wax is a vegetable wax which occurs as a protective coating on the leaves of a species of Brazilian palm. It is composed largely of myricyl cerotate, $C_{25}H_{51}.COOC_{31}H_{63}$. Its uses are similar to those of beeswax.

**8-3. Spermaceti wax.** This wax is obtained from the head cavity and blubber of the sperm whale, and consists chiefly of cetyl palmitate, $C_{15}H_{31}.COOC_{16}H_{33}$. It is used for pharmaceutical and cosmetic preparations.

**8-4. Differences between waxes and fats.** These are :

(1) The waxes are generally harder and less greasy than fats.

(2) The animal fats are esters of glycerol, a low molecular-weight trihydroxy alcohol; the waxes are esters of various high molecular weight long-chain monohydroxy alcohols.

(3) The fatty acids involved in fats may be saturated or unsaturated, those involved in waxes are essentially saturated acids.

### Questions

1. (*a*) What types of compounds are called acid derivatives, in general ? What are the main classes of acid derivatives ? Write their class names and formulas.

(*b*) How is acetyl chloride prepared in the laboratory ? Draw a neat, lebelled sketch of the apparatus used.

(*c*) How does acetyl chloride react with water, ethyl alcohol, ammonia, ethylamine, aniline, add anhydrous sodium acetate ?

(*d*) List the uses of acetyl chloride.

2. (*a*) How is acetic anhydride prepared in the laboratory ? On a large scale ?

(*b*) How does acetyl chloride react with water, ethyl alcohol, aniline, dry hydrogen chloride and phosphorus pentachloride ?

(*c*) Give the main uses of acetic anhydride.

3. (*a*) Describe the laboratory preparation of acetamide. Draw a neat, labelled sketch of the apparatus used.

(*b*) Why does acetamide melt and boil at higher temperatures than will be expected for a compound with a molecular weight of only 59.

(*c*) What happens when acetamide is—

*i*. boiled with an alkali solution,

*ii*. treated with bromine and sodium hydroxide,

*iii*. treated with nitrous acid,

*iv*. distilled with phosphorus pentoxide,

*v*. catalytically reduced ?

4. (*a*) What are esters ? How do they differ from salts ?

(*b*) How is ethyl acetate prepared in the laboratory ?

(*c*) What are the products of the hydrolysis of ethyl acetate ? What ions catalyse it ?

(*d*) Explain 'saponification' with a suitable example.

(*e*) What are the reactions of ethyl acetate with ammonia, phosphorus pentachloride, and lithium aluminium hydride ?

(*f*) What is the main industrial application of ethyl acetate ?

6. (*a*) What is the chemical nature of fats and oils, and what is the cause of difference in their physical state under ordinary conditions ?

(*b*) Give examples of simple glycerides and mixed glycerides.

(*c*) Give names of the chief products formed, and write the equations for what happens when—

*i*. oils and fats are heated with a solution of caustic soda,

*ii*. oils react with hydrogen in the presence of nickel at 250°C.

(*d*) Why do fats and oils become rancid on storage ?

7. (*a*) What is the chemical nature of soaps ?

(*b*) Describe the modern continuous process for soap-making.

(*c*) Explain the cleansing action of soaps.

8. (*a*) What is the chemical nature of animal and vegetable waxes ?

(*b*) Write the names and formulas of three acids and three alcohols which occur in waxes.

(*c*) In what respects do waxes differ from fats ?

□□

# 24

# Polyhydric Alcohols

*Alcohols containing two or more hydroxyl groups attached to different carbon atoms in the molecule are called polyhydric alcohols.* Often alcohols with two hydroxyl groups in the moleculeare called *dihydric alcohols, e.g.*, ethylene glycol, $CH_2OH.CH_2OH$, and those with three hydroxyl groups are called trihydric alcohols, *e.g.*, glycerol, $CH_2OH.CHOH.CH_2OH$.

Like the monohydric alcohols (*e.g.*, methyl alcohol and ethyl alcohol) studied earlier, the polyhydric alcohols are also derived from alkanes; of course, each $-OH$ group is linked to a different carbon atom in the alkane molecule. For example,

$$\begin{array}{ccc} CH_4\ \text{(methane)} & CH_3{-}CH_3\ \text{(ethane)} & CH_3{-}CH_2{-}CH_3\ \text{(propane)} \\ -H \big\downarrow +OH & -2H \big\downarrow +2OH & -3H \big\downarrow +3OH \\ CH_3OH & CH_2OH{-}CH_2OH & CH_2OH{-}CHOH{-}CH_2OH \\ \text{methyl alcohol} & \text{ethylene glycol} & \text{glycerol} \\ \text{(monohydric)} & \text{(dihydric)} & \text{(trihydric)} \end{array}$$

In general, the polyhydric alcohols possess the properties of the monohydric alcohols $n$ times, where $n$ is the number of hydroxyl groups in the molecule. As the value of $n$ increases, (*a*) the boiling point increases due to increasing molecular weight, (*b*) the solubility in water increases due to increased hydrogen bonding, and (*c*) sweetness increases.

In this chapter we shall study the trihydric alcohol, glycerol.

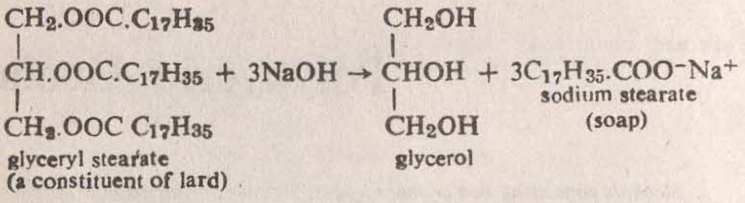
## 1. Glycerol, $C_3H_5(OH)_3$

Glycerol, the only important trihydric alcohol, occurs naturally as its esters (*glycerides*) with certain higher aliphatic acids (*e.g.*, palmitic, stearic, and oleic acids) in animal and vegetable oils and fats. It is also called trihydroxypropane. Its IUPAC name is 1, 2, 3-propanetriol.

Small quantities of glycerol (about 3%) are formed as a by-product in the alcoholic fermentation of sugar. The yield of glycerol can be substantially increased by the addition of sodium hydrogen sulphite to the fermenting solution. Even then, the yield of glycerol is not high enough for the process to be economically feasible under normal conditions.

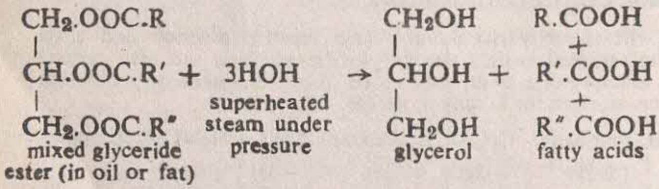
## 2. Manufacture of Glycerol

1. **By the hydrolysis of oils and fats.** Large quantities of glycerol are obtained as a by-product in the manufacture of soaps, the sodium salts of higher acids, by the hydrolysis of oils and fats with sodium hydroxide solution (*saponification*). For example,



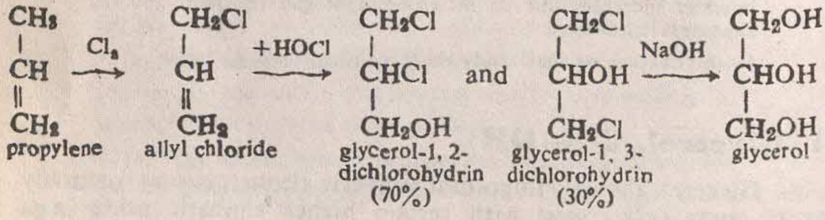
$$\underset{\substack{\text{glyceryl stearate}\\\text{(a constituent of lard)}}}{\begin{array}{l}\mathrm{CH_2.OOC.C_{17}H_{35}}\\ |\\ \mathrm{CH.OOC.C_{17}H_{35}}\\ |\\ \mathrm{CH_2.OOC\,C_{17}H_{35}}\end{array}} + \mathrm{3NaOH} \rightarrow \underset{\text{glycerol}}{\begin{array}{l}\mathrm{CH_2OH}\\ |\\ \mathrm{CHOH}\\ |\\ \mathrm{CH_2OH}\end{array}} + \underset{\substack{\text{sodium stearate}\\\text{(soap)}}}{\mathrm{3C_{17}H_{35}.COO^-Na^+}}$$

Sometimes, the oils and fats are hydrolysed with superheated steam under pressure when the products are free fatty acids and glycerol. For example,



$$\underset{\substack{\text{mixed glyceride}\\\text{ester (in oil or fat)}}}{\begin{array}{l}\mathrm{CH_2.OOC.R}\\ |\\ \mathrm{CH.OOC.R'}\\ |\\ \mathrm{CH_2.OOC.R''}\end{array}} + \underset{\substack{\text{superheated}\\\text{steam under}\\\text{pressure}}}{\mathrm{3HOH}} \rightarrow \underset{\text{glycerol}}{\begin{array}{l}\mathrm{CH_2OH}\\ |\\ \mathrm{CHOH}\\ |\\ \mathrm{CH_2OH}\end{array}} + \underset{\text{fatty acids}}{\begin{array}{c}\mathrm{R.COOH}\\ +\\ \mathrm{R'.COOH}\\ +\\ \mathrm{R''.COOH}\end{array}}$$

2. **By synthesis from propylene produced from cracking petroleum and natural gas.** Propylene is reacted with chlorine at 500° when the main product is allyl chloride. The latter is treated with hypochlorous acid when two isomeric glycerol dichlorohydrins are formed. These isomers are treated with sodium hydroxide when they are hydrolysed to glycerol.



$$\underset{\text{propylene}}{\begin{array}{l}\mathrm{CH_3}\\ |\\ \mathrm{CH}\\ \|\\ \mathrm{CH_2}\end{array}} \xrightarrow{\mathrm{Cl_2}} \underset{\text{allyl chloride}}{\begin{array}{l}\mathrm{CH_2Cl}\\ |\\ \mathrm{CH}\\ \|\\ \mathrm{CH_2}\end{array}} \xrightarrow{+\mathrm{HOCl}} \underset{\substack{\text{glycerol-1, 2-}\\\text{dichlorohydrin}\\(70\%)}}{\begin{array}{l}\mathrm{CH_2Cl}\\ |\\ \mathrm{CHCl}\\ |\\ \mathrm{CH_2OH}\end{array}} \text{ and } \underset{\substack{\text{glycerol-1, 3-}\\\text{dichlorohydrin}\\(30\%)}}{\begin{array}{l}\mathrm{CH_2Cl}\\ |\\ \mathrm{CHOH}\\ |\\ \mathrm{CH_2Cl}\end{array}} \xrightarrow{\mathrm{NaOH}} \underset{\text{glycerol}}{\begin{array}{l}\mathrm{CH_2OH}\\ |\\ \mathrm{CHOH}\\ |\\ \mathrm{CH_2OH}\end{array}}$$

## 3. Physical Properties of Glycerol

1. Glycerol is a colourless, odourless viscous liquid, which is very hygroscopic and has a sweetish taste.

2. It boils at 290°, often decomposing slightly.

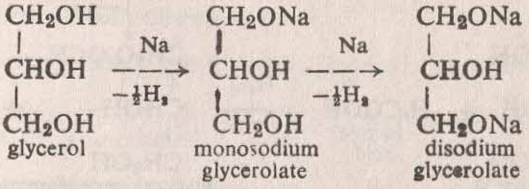
3. Anhydrous glycerol crystallizes (m.p. 18°C) when strongly cooled

4. It is miscible with water and ethanol in all proportions, but almost insoluble in ether.

## 4. Reactions of Glycerol

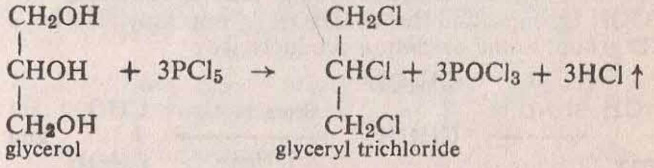
The chemical reactions of glycerol are essentially those expected of a trihydric alcohol. Thus, it reacts with sodium and forms mono-, di-, and tri-esters which are known as glycerides. Its important reactions are :

**1. With sodium.** With sodium first one primary alcoholic group ($-CH_2OH$) is attacked and then, on heating, the other one also, with the liberation of hydrogen. The secondary alcoholic group ($\triangleright CHOH$) is not attacked at all.



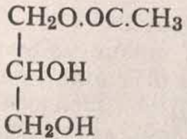
$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{glycerol} \end{array} \xrightarrow[-\frac{1}{2}H_2]{Na} \begin{array}{c} CH_2ONa \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{monosodium} \\ \text{glycerolate} \end{array} \xrightarrow[-\frac{1}{2}H_2]{Na} \begin{array}{c} CH_2ONa \\ | \\ CHOH \\ | \\ CH_2ONa \\ \text{disodium} \\ \text{glycerolate} \end{array}$$

**2. With phosphorus pentachloride.** Glycerol reacts, with phosphorus pentachloride to give glyceryl trichloride by the replacement of all three hydroxyl groups by chlorine atoms.



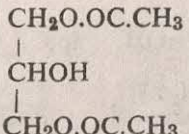
$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{glycerol} \end{array} + 3PCl_5 \rightarrow \begin{array}{c} CH_2Cl \\ | \\ CHCl \\ | \\ CH_2Cl \\ \text{glyceryl trichloride} \end{array} + 3POCl_3 + 3HCl\uparrow$$

**3. With acids** (*estrification*). Monocarboxylic acids react with one, two, or all three of the hydroxyl groups in each molecule of glycerol, giving esters called *glycerides*. Thus, with acetic acid (as also with acetic anhydride) mono-, di-, and tri-acetates are obtained.



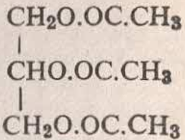
$$\begin{array}{c} CH_2O.OC.CH_3 \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

glyceryl monoacetate



$$\begin{array}{c} CH_2O.OC.CH_3 \\ | \\ CHOH \\ | \\ CH_2O.OC.CH_3 \end{array}$$

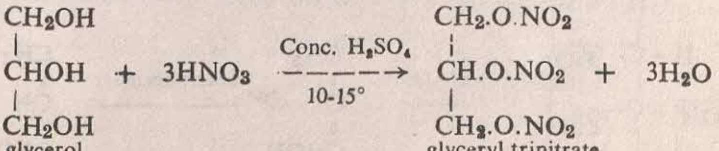
glyceryl diacetate



$$\begin{array}{c} CH_2O.OC.CH_3 \\ | \\ CHO.OC.CH_3 \\ | \\ CH_2O.OC.CH_3 \end{array}$$

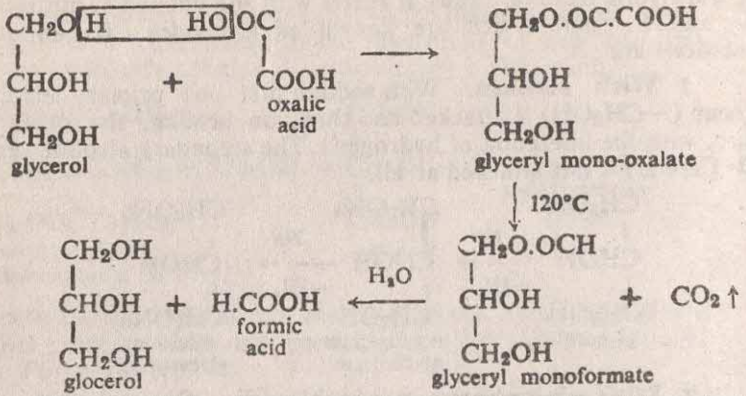
glyceryl triacetate

When glycerol is treated with a cold mixture of concentrated nitric and sulphuric acids, it is converted into the ester glyceryl trinitrate, commonly known as nitroglycerine.

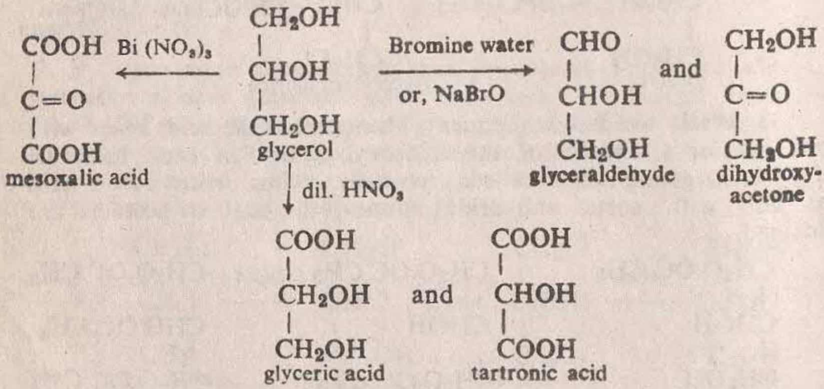


$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{glycerol} \end{array} + 3HNO_3 \xrightarrow[10\text{-}15^\circ]{\text{Conc. } H_2SO_4} \begin{array}{c} CH_2.O.NO_2 \\ | \\ CH.O.NO_2 \\ | \\ CH_2.O.NO_2 \\ \text{glyceryl trinitrate} \end{array} + 3H_2O$$

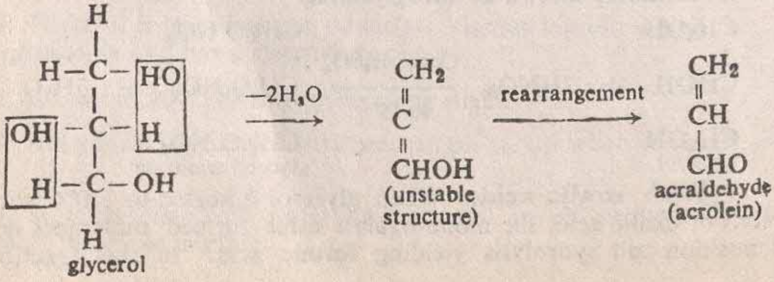
**4. With oxalic acid.** When glycerol is heated to 120°C with crystals of oxalic acid, the mono-oxalate ester formed undergoes decomposition and hydrolysis yielding formic acid. In this reaction glycerol is regenerated and it merely serves to bring about the decomposition of oxalic acid into formic acid.



5. **Oxidation.** On oxidation glycerol yields a variety of product depending on the oxidizing agents and the conditions used. Either one or both of the $-CH_2OH$ groups may be oxidized to $-CHO$ or $-COOH$ groups, and the $>CHOH$ group may also be oxidized to $>CO$ group. Some oxidation products are :



6. **Dehydration**. When heated alone, or with a dehydrating agent such as phosphorus pentoxide or concentrated sulphuric acid, glycerol loses two molecules of water to give acraldehyde, also called acrolein.



## 5. Tests for Glycerol

1. It is a colourless, viscous liquid, having a sweet taste.

2. When heated with concentrated sulphuric acid, glycerol yields acraldehyde which has a pungent odour.

3. When glycerol is added to 1 per cent borax solution rendered pink by the addition of a few drops of phenolphthalein, the pink colour disappears on warming but appears again on cooling.

## 6. Uses of Glycerol

Glycerol has found many wide-spread commercial applications.

1. *In pharmacy*, it is used in the manufacture of ointments, tooth-pastes and cosmetics.

2. *In the tobacco industry*, it is used as a humectant (moistening agent) to maintain the moisture content of the finished product.

3. *In the manufacture of alkyd resins**, which are important consituents of many modern varnishes and paints because they give a hard, glossy, protective finish.

4. *As a softening and moistening agent* in copying ink and printing ink, typewriter ribbons, leather goods, etc.

5. *In the explosive industry*, for the manufacture of nitroglycerine explosives, e. g., dynamite, blasting gelatine, cordite, etc.

6. *As an anifreeze material* in aqueous solution in car radiators and gas meters.

7. *As a hydraulic brake fluid*.

**6-1. Nitroglycerine explosives.** Nitroglycerine is manufactured by adding glycerol in a thin stream to a mixture of concentrated nitric acid and sulphuric acid, temperature being kept 10-15°C throughout. Glyceryl trinitrate, common name nitroglycerine** separates as colourless, viscous liquid in the upper layer.

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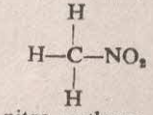
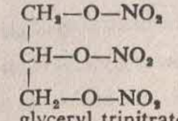
*These are made by reaction with phthalic anhydride.

**The name nitroglycerine is erroneous since the compound does not contain a nitro ($NO_2$) group directly attached through the N atom to a carbon atom.



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-NO_2$$

nitro-methane



$$\begin{array}{l} CH_2-O-NO_2 \\ | \\ CH-O-NO_2 \\ | \\ CH_2-O-NO_2 \end{array}$$

glyceryl trinitrate
(="nitroglycerine").

Glyceryl trinitrate is a powerful and treacherous explosive. In the pure form it is sensitive to heat or to a sharp blow. It is also used in the manufacture of the explosives given below :

1. *Dynamite.* It is made by mixing glyceryl trinitrate with ammonium nitrate, sodium nitrate, and wood pulp.

2. *Blasting gelatine.* It is made by soaking glyceryl trinitrate in cellulose nitrate (guncotton).

3. *Cordite.* It is made by mixing glyceryl trinitrate with gun cotton and vaseline. It is used as a *smokeless powder*.

Glyceryl trinitrate is used medicinally in the relief of the arterial spasms of angina pectoris.

## 7. Structure of Glycerol

1. The molecular formula of glycerol as deduced from its analytical data and molecular weight is $C_3H_8O_3$.

2. Its reactions with phosphorus pentachloride and acetic anhydride show the presence of three hydroxyl groups in the molecule.

3. Since it is a very stable compound, all the three hydroxyl groups must be attached to different carbon atoms. This gives the structural formula.

$$CH_2OH - CHOH - CH_2OH$$

4. The above structure is confirmed by its synthesis from prophylene, described on page 68.

### Questions

1. (*a*) What are polyhydric alcohols.

(*b*) Write the name and structural formulae of two polyhydric alcohols.

2. How is glycerol obtained from oils and fats? Give two reactions of glycerol with balanced chemical equations.

3. Give the various reaction involved in the synthesis of glycerol from propylene.

4. (*a*) Give the IPUAC name of glycerol.

(*b*) How does glycerol react with—

(*i*) phosphorus pentachloride,
(*ii*) oxalic acid, and
(*iii*) phosphorus pentoxide ?

(*c*) List the main uses of glycerol.

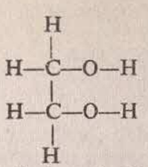
5. (*a*) How is glyceryl trinitrate made ?

(*b*) Name three explosives made from glyceryl trinitrate.

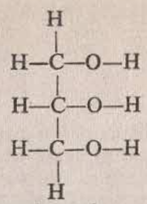
(*c*) Why is it wrong to name glyceryl trinitrate as nitroglycerine ?

## Key

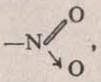
1. (*b*)

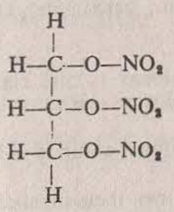


ethylene glycol



glycerol

5. (*c*) Nitro compounds have a nitro group, , directly linked through the N atom to a carbon atom in the molecule. In glyceryl trinitrate, the nitro groups are linked to the carbon atoms through oxygen atoms as shown below :



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# 25

# Aliphatic Nitrogen Compounds

## (Ethylamine, Urea, and Glycine)

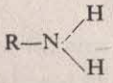
This chapter deals with three important aliphatic nitrogen compounds : ethylamine, urea (or, carbamide), and glycine (or amino-acetic acid).

**Ethylamine.** $C_2H_5.NH_2$ belongs to the class of aliphatic *primary amines* which form a homologous series with the general formula $C_nH_{2n+1}.NH_2$. Their functional group is $-N\begin{array}{l}\diagup H\\ \diagdown H\end{array}$, called the amino group, which determines their chemical behaviour, the alkyl radicals ($C_nH_{2n+1}^{-}$) being relatively inert.

Primary amines themselves belong to a larger group, *viz.* the aliphatic amines. These may be regarded as derivatives of ammonia, in which one, two, or three of the hydrogen atoms are replaced by alkyl radicals. If one hydrogen atom in ammonia is replaced by an aikyl radical the product is classed as a primary amine; replacement of two and three hydrogen atoms by alkyl groups gives secondary and tertiary amines respectively.*

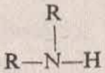
$NH_3$

ammonia



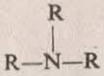
$R-N\begin{array}{l}\diagup H\\ \diagdown H\end{array}$

primary amine



$R-\overset{\overset{\displaystyle R}{|}}{N}-H$

secondary amine



$R-\overset{\overset{\displaystyle R}{|}}{N}-R$

tertiary amine

**Urea,** $O{=}C\begin{array}{l}\diagup NH_2\\ \diagdown NH_2\end{array}$ belongs to the class of acid amides, one member of which, *viz.*, acetamide has already been studied.

**Glycine,** $NH_2.CH_2.COOH$, also called aminoacetic acid, is a typical *amino-acid.* Amino-acids are compounds whose molecules contain both an amino group, $-NH_2$, and a carboxyl group,

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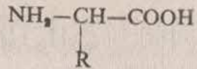
*The terms primary, secondary, and tertiary refer to the condition of nitrogen atom in the amines, and to the condition of carbon atom in alkyl halides and alcohols.

—COOH. The structures of other amino acids may be represented by the formula



$$NH_2-\underset{\displaystyle R}{\underset{|}{C}}H-COOH$$

where R is an alkyl radical. These may be regarded as carboxylic acids in whose molecules a hydrogen atom in the alkyl radical has been replaced by an amino group. Aminoacids are of great biochemical importance because from them are made all the complex protein molecules without which life is impossible.

## 1. Ethylamine, $C_2H_5.NH_2$

**1-1. Preparation.** Ethylamine can be prepared by following methods :

1. By heating ethyl iodide to 100°C in a sealed tube with a large excess of an alcoholic solution of ammonia. Ethylamine is formed as its hydroiodide.

$$\underset{\text{ethyl iodide}}{C_2H_5I} + \underset{\text{ammonia}}{NH_3} \rightarrow \underset{\text{ethylamine hydroiodide}}{C_2H_5.NH_2\,HI}$$

This method is not a good one because further reaction usually occurs giving secondary and tertiary amines as well.

$$\underset{\text{ethylamine}}{C_2H_5.NH_2} + \underset{\text{ethyl iodide}}{C_2H_5I} \rightarrow \underset{\text{diethylamine}}{(C_2H_5)_2NH} + HI$$

$$\underset{\text{diethylamine}}{(C_2H_5)_2NH} + \underset{\text{ethyl iodide}}{C_2H_5I} \rightarrow \underset{\text{triethylamine}}{(C_2H_5)_3N} + HI$$

2. By passing a mixture of ethyl alcohol vapour and excess ammonia over alumina heated to 350°C.

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} + NH_3 \rightarrow \underset{\text{ethylamine}}{C_2H_5.NH_2} + H_2O$$

This method, too, yields a mixture of ethylamine, diethylamine, and triethylamine which have to be separated.

3. By reducing acetamide with lithium aluminium hydride.

$$\underset{\text{acetamide}}{CH_3.CONH_2} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{ethylamine}}{CH_3.CH_2.NH_2} + H_2O$$

4. By reducing methyl cyanide with alcohol and metallic sodium or with lithium aluminium hydride.

$$\underset{\text{methyl cyanide}}{CH_3.CN} + 4[H] \xrightarrow{Na/alc.} \underset{\text{ethylamine}}{CH_3.CH_2.NH_2}$$

5. By the interaction of ethylmagnesium chloride (Grignard reagent) and chloramine.

$$\underset{\text{ethyl mag. chloride}}{C_2H_5.MgCl} + \underset{\text{chloramine}}{Cl.NH_2} \rightarrow \underset{\text{ethylamine}}{C_2H_5.NH_2} + MgCl_2$$

6. By the action of bromine and caustic potash on propionamide (*Hoffmann's degradation reaction*).

$$\underset{\text{propionamide}}{C_2H_5.CONH_2} + Br_2 + 4KOH \rightarrow \underset{\text{ethylamine}}{C_2H_5.NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

7. By reducing nitroethane with zinc and hydrochloric acid or by passing its vapour mixed with hydrogen over finely divided nickel at 150°C.

$$C_2H_5.NO_2 + 6[H] \rightarrow C_2H_5.NH_2 + 2H_2O$$

This method is unimportant as nitroalkanes are not easily prepared.

## 2. Laboratory Preparation of Ethylamine

Ethylamine is most conveniently prepared in the laboratory from propionamide by *Hoffmann's degradation reaction*, so called because the resulting amine contains one carbon atom less than the amide. The reaction proceeds in three steps :

1. Bromopropionamide is formed by substitution when bromine acts on propionamide.

$$\underset{\text{propionamide}}{C_2H_5.CONH_2} + Br_2 \rightarrow \underset{\text{bromopropionamide}}{C_2H_5.CONHBr} + HBr$$

2. The bromo derivative, when warmed with concentrated alkali to 70°C, loses hydrogen bromide and undergoes an internal rearrangement to ethyl isocyanate.

$$\underset{\text{bromopropionamide}}{C_2H_5.CONHBr} + KOH \rightarrow \underset{\text{ethyl isocyanate}}{C_2H_5.NCO} + KBr + H_2O$$

3. The isocyanate is then hydrolyzed by the hot alkali to give ethylamine.

$$\underset{\text{ethyl isocyanate}}{C_2H_5.NCO} + 2KOH \rightarrow \underset{\text{ethylamine}}{C_2H_5.NH_2\uparrow} + K_2CO_3$$

**Procedure**. Equivalent amounts of bromine and propionamide are cautiously mixed in a flask. A 10 per cent solution of caustic potash is slowly added until the colour of the bromine disappears. The mixture now contains bromopropionamide. To this is added an axcess of a concentrated aqueous solution of caustic potash. The contents of the flask are distilled on a water bath at 60°-70°C, and the ethylamine that distils over is absorbed in dilute hydrochloric acid (Fig. 23-1). The solution of ethylamine hydrochloride is evaporated to dryness on a water both to obtain it as a solid. If required, solid ethylamine hydrochloride is distilled with an alkali to obtain free ethylamine.

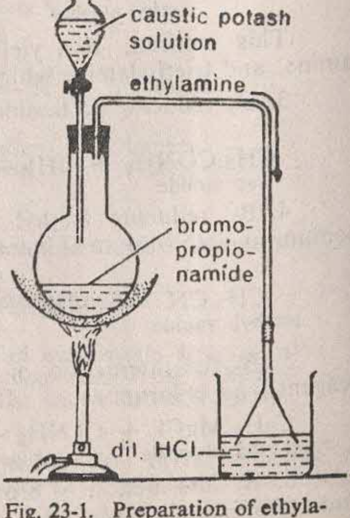


Fig. 23-1. Preparation of ethylamine from propionamide.

## 3. Manufacture of Ethylamine

Ethylamine is prepared on a large scale by heating ethylene with excess of ammonia under pressure at 400°C in the presence of a cobalt catalyst.

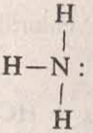
$$\underset{\text{ethylene}}{CH_2{=}CH_2} + \underset{\text{ammonia}}{HNH_2} \xrightarrow{\text{Co, }400^\circ\text{C}} \underset{\text{ethylamine}}{CH_3.CH_2.NH_2}$$

## 4. Physical Properties of Ethylamine

1. Ethylamine is a colourless substance, smelling like ammonia.
2. It boils at 17°C.
3. It is highly soluble in water and in organic solvents.

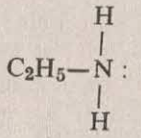
## 5. Reactions of Ethylamine

**1. As a base.** Owing to the presence of the lone pair of electrons on the nitrogen atom (as in ammonia molecule),



$$\begin{array}{c} H \\ | \\ H{-}N: \\ | \\ H \end{array}$$

(ammonia)



$$\begin{array}{c} \phantom{C_2H_5-}H \\ \phantom{C_2H_5-}| \\ C_2H_5{-}N: \\ \phantom{C_2H_5-}| \\ \phantom{C_2H_5-}H \end{array}$$

(ethylamine)

ethylamine can accept a proton and form an ion resembling the ammonium ion. As such, ethylamine reacts with water forming ethylammonium hydroxide which ionizes to give hydroxyl ion in solution.

$$\underset{\text{ethylamine}}{C_2H_5.NH_2} + H_2O \rightleftharpoons \underset{\substack{\text{ethylammonium}\\ \text{hydroxide}}}{C_2H_5.NH_3OH} \rightleftharpoons C_2H_5.NH_3^+ + OH^-$$

(compare with $NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$)

Its aqueous solution is therefore alkaline, turns blue litmus red, and precipitates insoluble metallic hydroxide (*e.g.*, ferric hydroxide from ferric chloride solution).

(*i*) Being weakly basic, ethylamine readily forms salts with strong acids, *e.g.*, ethylamine hydrochloride with hydrochloric acid.

$$\underset{\text{ethylamine}}{C_2H_5.NH_2} + HCl \rightarrow \underset{\text{ethylamine hydrochloride}}{[C_2H_5.NH_3]^+Cl^-}$$

This salt is also formulated as $C_2H_5.NH_2.HCl$ or $C_2H_5.NH_3Cl$. The salts of ethylamine are colourless crystalline compounds, readily soluble in water. When these are heated with alkalis, ethylamine is set free.

$$C_2H_5.NH_3Cl + NaOH \xrightarrow{\Delta} C_2H_5.NH_2 + NaCl + H_2O$$

(*ii*) Ethylamine combines with chloroplatinic acid, $H_2PtCl_6$, forming sparingly soluble ethylamine chloroplatinate, $(C_2H_5.NH_2)_2.PtCl_6$. The latter, when ignited, leaves a residue of pure platinum.

2. *Alkylation.* When an alcoholic solution of ethylamine is heated with an alkyl halide in a sealed tube, the hydrogen atoms of the ammonia residue (*i.e.*, the $-NH_2$ group) are successively replaced by alkyl groups. Thus ethylamine reacts with ethyl iodide to give the following products :

$$C_2H_5.NH_2 + C_2H_5I \longrightarrow \underset{\text{diethylamine hydroiodide}}{(C_2H_5)_2NH.HI}$$

$$(C_2H_5)_2NH.HI + C_2H_5I \longrightarrow \underset{\text{triethylamine hydroiodide}}{(C_2H_5)_3N.HI} + HI$$

$$(C_2H_5)_3N.HI + C_2H_5I \longrightarrow \underset{\text{tetraethylammonium iodide}}{(C_2H_5)_4NI} + HI$$

3. *Acetylation.* Ethylamine is readily acetylated by acetyl chloride and acetic anhydride in the cold to give ethyl acetamide.

$$\underset{\text{ethylamine}}{C_2H_5.NH_2} + CH_3.COCl \rightarrow \underset{\text{ethyl acetamide}}{C_2H_5.NH.COCH_3} + HCl\uparrow$$

4. *Benzoylation.* Ethylamine reacts with benzoyl chloride in the presence of an alkali solution to give ethyl benzamide.

$$\underset{\text{ethylamine}}{C_2H_5.NH_2} + \underset{\text{benzoylchloride}}{C_6H_5.COCl} \xrightarrow{\text{alk.}} \underset{\text{ethyl benzamide}}{C_2H_5.NH.CO.C_6H_5} + HCl$$

5. *With nitrous acid.* When ethylamine is treated with nitrous acid (*i.e.*, an acidified solution of sodium nitrite), its $-NH_2$ group is replaced by $-OH$ group, yielding ethyl alcohol.

$$\underset{OH}{C_2H_5}\,|\,\underset{N}{N}\,|\,\underset{O}{H_2} + HNO_2 \rightarrow C_2H_5OH + H_2O + N_2\uparrow$$

6. *Isocyanide reaction.* When ethylamine is warmed with chloroform and alcoholic caustic potash solution, ethyl isocyanide is formed which is easily recognized by its very persistent and extremely offensive odour.

$$\underset{\text{ethylamine}}{C_2H_5.NH_2} + \underset{\text{chloroform}}{CHCl_3} + 3KOH \rightarrow \underset{\text{ethyl isocyanide}}{C_2H_5.NC} + 3KCl + 3H_2O$$

This reaction serves as a very delicate test for a primary amine (both aliphatic and aromatic).

7. *With sodium.* When heated with sodium, ethylamine yields a monosodium derivative.

$$2C_2H_5.NH_2 + 2Na \xrightarrow{\Delta} 2C_2H_5NH.Na + H_2\uparrow$$

## 6. Comparison Between Ethylamine and Ammonia

**6-1. Points of similarity.** These may be summarized as follows :

*i. Action with water.* Both dissolve, and give $OH^-$ ion in solution.

*ii. Action with ferric chloride solution.* Both give a reddish-brown precipitate of $Fe(OH)_3$.

*iii. Action with copper sulphate solution.* Both give a deep blue solution containing the complex ions $[Cu(NH_3)_4]^{2+}$ and $[Cu(C_2H_5.NH_2)_4]^{2+}$ respectively.

*iv. Salt formation.* Both form salts with acids, *e.g.*, $NH_4Cl$ and $C_2H_5.NH_3Cl$; $(NH_4)_2SO_4$ and $(C_2H_5.NH_3)_2SO_4$; both give white fumes with HCl.

*v. Alkylation.* Both react with ethyl halides to give a mixture of primary, secondry, and tertiary amines, and a quaternary compound.

*vi. Acetylation.* Both react with acetyl chloride and acetic anhydride; ammonia gives acetamide, ethylamine gives ethyl acetamide.

*vii. Action with sodium.* Both react with sodium yielding similar sodium derivatives.

$$2C_2H_5.NH_2 + 2Na \rightarrow 2C_2H_5.NHNa + H_2$$

$$2NH_3 + 2Na \rightarrow 2NaNH_2 + H_2$$

6-2. **Points of difference.** These are :

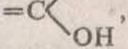
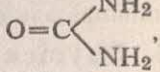
*i. Action with nitrous acid.* Ethylamine gives ethyl alcohol, water and nitrogen; ammonia gives only water and nitrogen.

$$C_2H_5.NH_2 + HNO_2 \rightarrow C_2H_5OH + H_2O + N_2\uparrow$$

$$NH_3 + HNO_2 \rightarrow NH_4NO_2 \rightarrow 2H_2O + Na\uparrow$$

*ii. Isocyanide reaction.* This reaction is given by ethylamine but not by ammonia.

## 7. Urea, Carbamide, $NH_2.CO.NH_2$

Urea is a derivative of carbonic acid,  $O{=}C(OH)_2$, in which both hydroxyl groups have been replaced by amino groups. Thus it is a *diamide* of carbonic acid with the structure,  $O{=}C(NH_2)_2$, which is why it is sometimes called *carbamide*. It is the nitrogenous end product of protein metabolism, and the adult human excretes about 30g of it a day in the urine. Urea has a great historical significance as the first ever organic compound synthesized in the laboratory (Wohler, 1828).

7-1. **Preparation of urea.** The various methods are :

1. *From urine.* On adding nitric acid to urine concentrated by evaporation to a small bulk, the sparingly soluble urea nitrate is precipitated. It is separated and treated with barium carbonate to liberate urea, which is extracted with alcohol.

$$2CO(NH_2)_2.HNO_3 + BaCO_3 \rightarrow 2CO(NH_2)_2 + Ba(NO_3)_2 + H_2O + CO_2.$$

2. *By the interaction of ammonia and carbonyl chloride, $COCl_2$, or ethyl carbonate, $(C_2H_5)_2CO_3$.*

$$\underset{\text{ammonia}}{NH_2}\boxed{H + Cl}\underset{\substack{\text{carbonyl}\\ \text{chloride}}}{CO}|\overline{Cl + H}|\underset{\text{ammonia}}{NH_2} \rightarrow \underset{\text{urea}}{NH_2.CO.NH_2} + 2HCl$$

$$\underset{\text{ammonia}}{NH_2}|\overline{H + C_2H_5O}|\underset{\text{ethyl carbonate}}{.CO.}|\overline{OC_2H_5 + H}|\underset{\text{ammonia}}{NH_2} \rightarrow \underset{\text{urea}}{NH_2CO.NH_2} + \underset{\text{ethyl alcohol}}{2C_2H_5OH}$$

3. *From ammonium cyanate* (**Laboratory preparation**). Ammonium sulphate and potassium cyanate are dissolved in equimolecular proportions in water, and the solution evaporated to dryness. Ammonium cyanate formed by double decomposition undergoes an isomeric change into urea.

$$\underset{\text{ammonium sulphate}}{(NH_4)_2SO_4} + \underset{\text{pot. cyanate}}{2KNCO} \rightleftharpoons \underset{\text{am. cyanate}}{2NH_4.NCO} + K_2SO_4$$

$$NH_4.NCO \rightleftharpoons NH_2.CO.NH_2$$

Although theoretically reversible, these changes proceed continuously to the right because urea crystallizes out as the solution is evaporated and is removed from the equilibrium. The solid residue consists, therefore, of urea and potassium sulphate. The urea is extracted from this mixture with hot absolute alcohol in which potassium sulphate is insoluble. The alcoholic solution deposits urea on cooling.

3. *By the interaction of carbon dioxide and ammonia* (**Manufacture**). A mixture of dry ammonia and carbon dioxide (3 : 1) is heated to 150° C under about 200 atmosphers pressure. Ammonium carbamate is first formed which loses water and changes to urea.

$$CO_2 + NH_3 \xrightarrow[\substack{200\\ \text{atm.}}]{150^\circ\text{ C}} \underset{\substack{\text{unstable car-}\\ \text{bamic acid}}}{NH_2.COOH} \xrightarrow{NH_3} \underset{\substack{\text{ammonium}\\ \text{carbamate}}}{NH_2.COONH_4} \xrightarrow{-H_2O} \underset{\text{urea}}{NH_2.CO.NH_2}$$

The reaction is conducted in steel reactors of the column type. Ammonium carbamate, if heated in the open, dissociates into ammonia and carbon dioxide.

## 8. Physical Properties of Urea

1. Urea is a colourless and odourless solid, m.p. 132°C. It is somewhat hygroscopic.

2. It dissolves freely in water and in hot alcohol, but is insoluble in ether or benzene.

## 9. Reactions of Urea

1. *Hydrolysis.* Urea is rapidly hydrolyzed into ammonia and carbon dioxide when boiled with solutions of acids or alkalis, or when heated with steam under pressure.

$$NH_2.CO.NH_2 + H_2O \rightarrow 2NH_3 + CO_2$$

$$NH_2.CO.NH_2 + 2NaOH \rightarrow 2NH_3 + Na_2CO_3$$

When treated with *urease*, an enzyme found in soyabeans, urea is rapidly hydrolyzed to ammonium carbonate, $(NH_4)_2CO_3$.

$$NH_2.CO.NH_2 + 2H_2O \rightarrow (NH_4)_2CO_3$$

This reaction, being quantitative, is used for estimating urea in solution.

The decomposition of urea, with the evolution of ammonia, also occurs in the 'ammoniacal fermentation' of urine under the influence of micro-organisms.

2. *Salt-formation*. Owing to its amino groups, urea displays the properties of a weak base, and forms salts with acids. For example, it forms urea nitrate. $[NH_2.CO.NH_2].HNO_3$, with nitric acid and urea oxalate, $[NH_2.CO.NH_2]_2.(COOH)_2.2H_2O$, with oxalic acid. These salts are only sparingly soluble in water and appear as white crystalline precipitates when concentrated solutions are mixed.

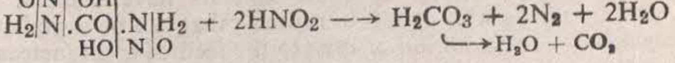
The aqueous solution of urea, however, is neutral to litmus.

3. *Action of heat*. When slowly heated urea first melts to a clear liquid and then two molecules of it give off a molecule of ammonia to give *biuret*.

$$\underset{\text{urea}}{NH_2.CO.}\boxed{NH_2+H}\underset{\text{urea}}{NH.CO.NH_2} \xrightarrow{\Delta} \underset{\text{biuret}}{NH_2.CO.NH.CO.NH_2} + NH_3\uparrow$$

The solution of biuret in dilute sodium hydroxide solution gives a violet-pink colour with one drop of very dilute (1%) copper sulphate solution. This reaction, called *biuret reaction*, is given by all compounds containing the $-CO.NH-$ group.

4. *With nitrous acid*. Urea reacts with nitrous acid (*i.e.*, acidified sodium nitrite solution) to give nitrogen, carbon dioxide, and water. In this reaction the two amino groups of urea are replaced by two hydroxyl groups to form carbonic acid, which at once decomposes into carbon dioxide and water.



$$\overset{O}{H_2}\Big|\overset{N}{N}\Big|.\underset{HO}{\overset{OH}{CO}}\Big|.\underset{N}{N}\Big|\underset{O}{H_2} + 2HNO_2 \longrightarrow H_2CO_3 + 2N_2 + 2H_2O$$
$$\hookrightarrow H_2O + CO_2$$

Or, $$NH_2.CO.NH_2 + 2HNO_2 \rightarrow 2N_2\uparrow + CO_2\uparrow + 3H_2O$$

5. *With sodium hypochlorite or hypobromite*. When urea is treated with excess of alkaline sodium hypochlorite (or hypobromite), nitrogen is evolved in the reaction :

$$NH_2.CO.NH_2 + 3NaCCl + 2NaOH \rightarrow N_2\uparrow + Na_2CO_3 + 3NaCl + 3H_2O$$

The yield of nitrogen is slightly less than would be expected from the equation. However, this reaction is used for the rough estimation of urea (in urine, for example) by measuring the volume of nitrogen evolved.

6. *Acetylation.* Urea reacts with acetyl chloride and acetic anhydride to give acetyl urea.

$$\underset{\text{acetyl chloride}}{CH_3.CO\boxed{Cl\ +\ H}}\underset{\text{urea}}{NH.CO.NH_2} \rightarrow \underset{\text{acetyl urea}}{CH_3.CO.NH.CO.NH_2} + HCl$$

7. *With hydrazine.* Urea reacts with hydrazine, $NH_2.NH_2$, to give semicarbazide.

$$\underset{\text{urea}}{NH_2.CO.\boxed{NH_2\ +\ H}}\underset{\text{hydrazine}}{NH.NH_2} \rightarrow \underset{\text{semicarbzaide}}{NH_2.CO.NH.NH_2} + NH_3 \uparrow$$

## 10. Tests for Urea

1. When urea is heated alone or with sodium hydroxide solution, ammonia is evolved.

2. When treated with acidified sodium nitrite solution or with bromine water and caustic soda (this gives sodium hypobromite, NaBrO) urea gives off nitrogen in cold.

3. Biuret reaction also serves as a test for urea. Urea is gently heated until ammonia is no longer evolved. The solid residue is cooled, dissolved in sodium hydroxide solution to which is added one drop of 1% copper sulphate solution. A violet-pink colour is produced.

4. When a concentrated solution of urea is treated with concentrated nitric acid or a concentrated solution of oxalic acid, a crystalline precipitate of urea nitrate or urea oxalate is formed.

## 11. Uses of Urea

1. *In farming.* Urea is extensively used in farming *as a nitrogenous fertilizer.* Its nitrogen content (47%) is much higher than that of other fertilizers, *e.g.*, ammonium sulphate, etc. Besides it is less hygroscopic, is easily dispersed, and does not make soils acidic. In the soil it is first converted by some soil bacteria into $NH_3$ and then to nitrates which are assimilated by plants.

2. *As a constituent of cattle foods.* Urea, to the extent of up to 33 per cent, is added to the normal protein feed of cattle and sheep. The digestive tracts of these animals have bacteria which convert the nitrogen of urea into proteins that can be assimilated by the organism. The addition of urea to the feed of cows increases the milk, while in the case of calves and sheep it considerably increases their weight.

3. *In chemical industry.* Large quantities of urea are used *for making urea-formaldehyde plastics.* These plastics are needed for plastic mouldings, and for imparting crease resistance to textiles, and also serve as adhesives in plywood and laminated plastics.

4. *In pharmaceutical industry.* Urea is used for making various hypnotics or sleep-inducing drugs, *e.g.*, veronal.

## 12. Glycine, Aminoacetic Acid, $NH_2.CH_2.COOH$

Glycine is the simplest of all amino acids. It occurs combined in bile acids and in many proteins. It represents nearly one-third of silk and one-tenth of wool.

**12-1. Preparation.** Glycine can be prepared by the following methods :

1. *By the interaction of chloroacetic acid and ammonia.* Chloroacetic acid is slowly added to a large excess of a concentrated solution of ammonia at room temperature. The chlorine atom in the acid is replaced by $NH_2$ group forming glycine, which combines with excess ammonia to form ammonium aminoacetate.

$$\underset{\text{chloracetic acid}}{Cl.CH_2.COOH} + 3NH_3 \rightarrow \underset{\text{ammonium aminoacetate}}{NH_2.CH_2.COONH_4} + NH_4Cl$$

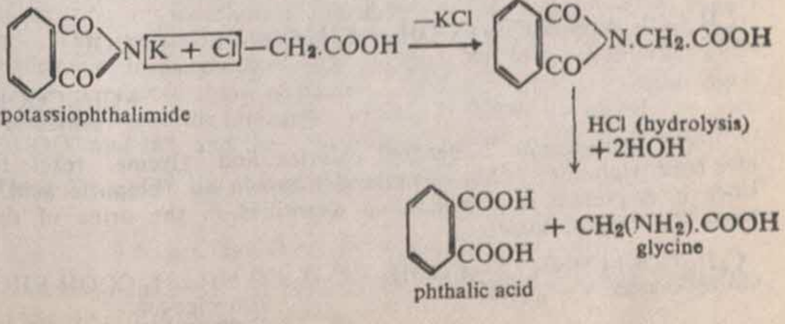
The reaction mixture is boiled with freshly precipitated copper hydroxide, and the slightly soluble cupric aminoacetate separated by fractional crystallization.

$$\underset{\text{ammonium aminoacetate}}{2NH_2.CH_2.COONH_4} + Cu(OH)_2 \xrightarrow{\Delta} \underset{\text{cupric aminoacetate}}{(NH_2.CH_2.COO)_2Cu} + 2H_2O + 2NH_3\uparrow$$

The crystals of cupric aminoacetate are dissolved in water and treated with hydrogen sulphide when free aminoacetic acid (glycine) is formed in solution and copper sulphide is precipitated. The latter is filtered off and the filtrate concentrated until glycine crystallizes out on cooling.

$$(NH_2.CH_2.COO)_2Cu + H_2S \rightarrow 2NH_2.CH_2.COOH + CuS\downarrow$$

2. *Gabriel's phthalimide synthesis.* Phthalimide is treated with caustic potash when it is converted into potassiophthalimide. The latter is heated with chloroacetic acid and the product hydrolysed by heating with 20 per cent hydrochloric acid under pressure to phthalic acid and glycine.



## 13. Physical Properties of Glycine

1. Glycine is colourless, crystalline substance, p.m. 233°C (with decomposition).

2. It is readily soluble in water but relatively insoluble in organic solvents such as alcohol and ether.

3. It has a sweet taste for which reason it was called glycocoll (*glykyl*, sweet; *kolla* glue).

4. It gives a deep red coloration with ferric chloride.

## 14. Reactions of Glycine

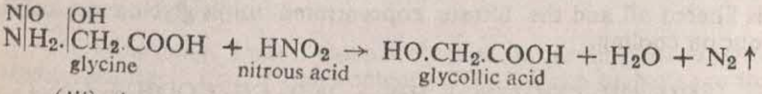
1. **Reactions of the amino group.** These are :

(*i*) *Salts with acids.* Glycine forms salts with acids, *e.g.*, glycine hydrochloride with hydrochloric acid.

$$\underset{\text{glycine}}{H_2N.CH_2.COOH} + HCl \rightarrow \underset{\text{glycine hydrochloride}}{[H_3N.CH_2.COOH]^+Cl^-}$$

Such salts dissolve in water to give solutions whose *p*H values are higher than those of the glycine solutions. This is because the basicity of the amino group has been neutralized, making the acidic character of the carboxyl group quite pronounced.

(*ii*) *With nitrous acid.* The primary amino group in glycine reacts with nitrous acid in the usual manner, being replaced by hydroxyl group with evolution of nitrogen. The product is glycollic acid.



$$\underset{\text{glycine}}{\begin{array}{c|c|l} N & O & OH \\ N & H_2. & CH_2.COOH \end{array}} + \underset{\text{nitrous acid}}{HNO_2} \rightarrow \underset{\text{glycollic acid}}{HO.CH_2.COOH} + H_2O + N_2\uparrow$$

(*iii*) *Acetylation.* When glycine is heated with acetyl chloride or acetic anhydride, the amino group is acetylated in the usual manner forming acetylglycine.

$$\underset{\text{acetyl chloride}}{CH_3.CO\boxed{Cl + H}}NH.\underset{\text{glycine}}{CH_2.COOH} \xrightarrow{\Delta} \underset{\text{acetylglycine}}{CH_3.CO.NH.CH_2.COOH} + HCl\uparrow$$

$$\underset{\text{acetic anhydride}}{(CH_3CO)_2} + \underset{\text{glycine}}{H_2N.CH_2.COOH} \xrightarrow{\Delta} \underset{\text{acetylglycine}}{CH_3.CO.NH.CH_2.COOH}$$

$$+\underset{\text{acetic acid}}{CH_3.COOH}$$

(*iv*) *Benzoylation.* Benzoyl chloride and glycine react to give benzoylglycine. This compound is known as "hippuric acid," since it is present in considerable quantities in the urine of the horse (Gr. *hippos*, horse).

$$\underset{\text{benzoyl chloride}}{C_6H_5.COCl} + \underset{\text{glycine}}{HNH.CH_2.COOH} \rightarrow \underset{\substack{\text{benzoylglycine}\\ \text{(hippuric acid)}}}{C_6H_5.CO.NH.CH_2.COOH} + HCl$$

**2. Reactions of the carboxyl group.** These are :

(*i*) *Salts with bases.* Glycine forms salts with bases.

$$NH_2.CH_2.COOH + NaOH \rightarrow NH_2.CH_2.COONa + H_2O$$

It reacts with copper to give deep blue copper glycine or copper aminoacetate.

$$\underset{\text{glycine}}{2NH_2.CH_2.COOH} + CuCO_3 \rightarrow \underset{\text{copper glycine}}{(NH_2.CH_2.COO)_2Cu} + H_2O + CO_2\uparrow$$

(*ii*) *Decarboxylation.* When heated in an unreactive solvent or when boiled with barium hydroxide solution, glycine loses carbon dioxide yielding methylamine, $CH_3.NH_2$.

$$NH_2.CH_2.COOH \xrightarrow{\Delta} CH_3.NH_2 + CO_2\uparrow$$

$$NH_2.CH_2.COOH + Ba(OH)_2 \longrightarrow CH_3.NH_2 + BaCO_3\downarrow + H_2O$$

(*iii*) *Esters with alcohols.* Glycine is esterified by boiling with alcohol in the presence of hydrogen chloride.

$$\underset{\text{aminoacetic acid}}{NH_2.CH_2.CO}\boxed{OH + H}\underset{\text{ethyl alcohol}}{OC_2H_5} \xrightarrow{HCl} \underset{\text{ethyl aminoacetate}}{NH_2.CH_2.COOC_2H_5} + H_2O$$

In fact, the hydrochloride of the ester is first formed from which the free ester is liberated by treatment with AgOH.

$$NH_2.CH_2.COOC_2H_5.HCl + AgOH \rightarrow NH_2.CH_2.COOC_2H_5 + AgCl\downarrow + H_2O$$

(*iv*) *Amide formation.* The ethyl ester of glycine reacts with ammonia to give glycine amide.

$$\underset{\text{ethyl ester of glycine}}{NH_2.CH_2.COOC_2H_5} + NH_3 \rightarrow \underset{\text{glycine amide}}{NH_2.CH_2.CO.NH_2} + \underset{\text{ethyl alcohol}}{C_2H_5OH}$$

**3. Interaction of amino and carboxyl groups**

(*i*) *Formation of zwitter ion.* Glycine has melting point which is much higher than its molecular size would indicate (*e.g.*, chloroacetic melts at 63°C, glycine at 233°C with decomposition). It is readily soluble in water, but relatively insoluble in organic solvents. These properties corresponding to inorganic ionic compounds rather than organic compounds are due to the fact that glycine is capable of existing in ionic salt-like form also called *dipolar ion* or *zwitter ion*. This becomes possible because the carboxyl group has a tendency to lose a proton (acidic character) and the amino group to accept a proton (basic character). The *inner salt* or *zwitter ion* is formed owing to the ionization of the —COOH group to the ions —$COO^-$ and $H^+$, and the migration of the $H^+$ to the —$NH_2$ group which changes to the charged —$\overset{+}{N}H_3$ group.

$$NH_2.CH_2.COOH \rightleftharpoons \overset{+}{N}H_3.CH_2.COO^-$$

In water solution both of these forms exist in equilibrium with the zwitter ion form predominating.

(*ii*) *Isoelectric point*. The zwitter ion may either lose or gain a proton, thus acting as an acid or as a base. In water solution the zwitter ion of glycine tends to lose a proton; hence, the negative glycine ion migrates to the anode when the solution is electrolyzed.

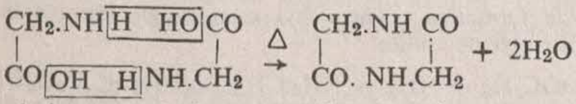
$$\underset{\text{zwitter ion}}{{}^{+}NH_3.CH_2.COO^-} + H_2O \rightleftharpoons \underset{\substack{\text{negative glycine ion}\\\text{(to the anode)}}}{[NH_2,CH_2.COO]^-} + H_3O^+$$

When hydrochloric acid, or other mineral acid is added, the zwitter ion is converted into a positive ion which migrates to the cathode during electrolysis.

$$\underset{\text{zwitter ion}}{{}^{+}NH_3.CH_2.COO^-} + H_3O^+ \rightleftharpoons \underset{\substack{\text{possitive glycine ion}\\\text{(to the cathode)}}}{[NH_3.CH_2.COOH]^+} + H_2O$$

Apparently, glycine will form either an anion or cation, depending upon the *p*H of the solution. At the *p*H value 6·0, glycine has equal tendencies to form either of these ions; hence its net charge is zero, and the ion does not move in either direction. This *p*H value is known as the *isoelectric point* of glycine. Every amino acid, in fact, has a definite isoelectric point, and for monoamino monocarboxylic acids, $NH_2\text{—}\underset{\substack{|\\ R}}{CH}\text{—}COOH$, this value is approximately 6.

(*iii*) *Effect of heat*. When glycine is heated, it loses water and forms a cyclic diamide, known as a diketopiperazine.



$$\begin{array}{l} CH_2.NH\boxed{H\ \ HO}CO \\ |\qquad\qquad\qquad\ | \\ CO\boxed{OH\ \ H}NH.CH_2 \end{array} \xrightarrow{\Delta} \begin{array}{l} CH_2.NH\ CO \\ |\qquad\qquad\ | \\ CO.\ NH.CH_2 \end{array} + 2H_2O$$

glycine glycine diketopiperazine

## 15. Uses of Glycine

Glycine funds use in photography, in the manufacture of resins and varnishes, and in preparing certain drugs.

### Questions

1. (*a*) Give three reactions for the preparation of aliphatic primary amines.

(*b*) Describe the preparation af ethylamine in the laboratory by Hoffmann's degradation reaction.

(*c*) Why does ethylamine act as a base? Give three reactions to illustrate the basic character of ethylamine.

2. What happens when ethylamine is—

(*a*) heated with an alkyl halide in alcoholic solution in a sealed tube,

(*b*) treated with acetyl chloride or acetic anhydride,

(*c*) treated with benzoyl chloride and alkali solution,

(*d*) treated with sodium nitrite and dilute hydrochloric acid.

(*e*) heated with chloroform and alc. KOH,

(*f*) heated with sodium metal?

3. Compare and contrast the properties of ethylamine and ammonia.

4. (*a*) Why is urea described as the diamide of carbonic acid? What is the historical importance of this compound in the realm of organic chemistry?

(*b*) Describe the laboratory preparation of urea from ammonium cyanate.

(*c*) Describe the manufacture of urea from ammonia and carbon dioxide.

(*d*) How would you establish that urea has the properties of a weak base?

5. (*a*) Describe the reactions of urea under the following headings :

(*i*) hydrolysis
(*ii*) action of heat
(*iii*) with nitrous acid
(*iv*) with sodium hypochlorite
(*v*) acetylation
(*vi*) with hydrazine.

(*b*) Which of the above reaction is commonly employed as a test for urea?

(*c*) List the main uses of urea.

6. (*a*) What is the chemical name for glycine? How is it prepared by Gabriel's phthalimide reaction?

(*b*) Give the reactions of glycine pertaining to (*i*) the $—NH_2$ group and (*ii*) the —COOH group.

(*c*) What happens when glycine is heated?

7. Write explanatory notes on :

(*i*) Zwitter ion
(*ii*) Isoelectric point
(*iii*) Biuret test.

□ □

# 26

# Optical Isomerism

Isomerism refers to the existence of two or more chemical compounds having the same molecular formula but a different arrangement of atoms within the molecule of each one. There are two main types of isomerism, structural isomerism and stereoisomerism. In structural isomerism (I.S.C. Chemistry Vol. I, page 3.37), the isomers have atoms linked in different ways; in stereoisomerism, the same atoms are linked together in the same way but are arranged differently in space.

Stereoisomerism is mainly of two kinds : cis-trans or geometrical isomerism which is shown by certain organic compounds containing double bond*, and optical isomerism which occurs in compounds with asymmetric carbon atoms. Unlike the geometrical isomers which differ in physical properties, chemical properties, and stability, the optical isomers have physical and chemical properties which are alike; they differ in the phenomenon known as optical activity and in their physiological activity.

## 1. Optical Isomerism

*The phenomenon of a chemical compound existing in two different forms having opposite effect on polarized light is called* **optical isomerism**, *while the different forms are called* **optical isomers** or **enantiomorphs**. The optical isomers are very similar in ordinary physical and chemical properties but usually differ markedly in biological behaviour.

**1-1. What is plane polarized light** ? Ordinary white light consists of electromagnetic radiations of different wavelengths vibrating in a number of planes. When it is passed through a suitable

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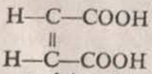
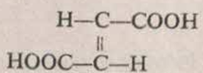
*Two examples of such compounds, *i.e.*, geometrical isomers are :



$$\begin{array}{l} H\text{—}C\text{—}COOH \\ \quad\;\, \| \\ H\text{—}C\text{—}COOH \end{array}$$

maleic acid

and



$$\begin{array}{r} H\text{—}C\text{—}COOH \\ \| \quad\quad\;\; \\ HOOC\text{—}C\text{—}H \end{array}$$

fumaric acid

m.p. 130°C, sp. gr. 1.59

m.p. 287°C, sp. gr. 1.64

filter, the outcoming light is of a single wavelength and is called monochromatic light. Monochromatic light, too, vibrates in all possible planes perpendicular to the direction of the light path (Fig. 26-1). *Plane polarized light refers to light waves which are vibrating in only one plane*, say vertically up and down (Fig. 26-2). It is obtained by passing monochromatic light through a Nicol prism (so named after the inventor William Nicol), made by cementing together two prisms of calcite* with Canada balsam.

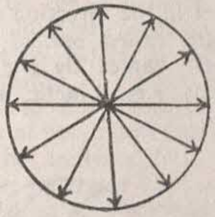


Fig. 26-1. Ordinary light.

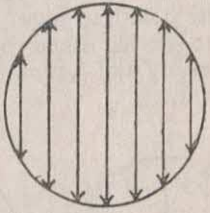


Fig. 26-2. Plane polarized light.

When monochromatic light enters the Nicol prism, it is split up into two rays, each vibrating in one plane only. One of these rays undergoes total internal reflection, while the other one is transmitted straight as plane-polarized light (Fig. 26-3). The plane-polarized light thus obtained vibrates in a plane at right angles to the reflected ray. If the plane polarized light is vibrating in the vertical plane only, the horizontal plane is termed the *plane of polarization*.

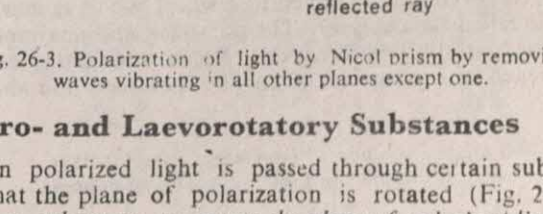


Fig. 26-3. Polarization of light by Nicol prism by removing waves vibrating in all other planes except one.

## 2. Dextro- and Laevorotatory Substances

When polarized light is passed through certain substances, it is found that the plane of polarization is rotated (Fig. 26-3). *The ability of a substance to rotate the plane of polarized light is called optical activity, while that substance is said to be optically active.* An optically active substance which rotates the plane of polarized light to the right is termed *dextrorotatory* (right-turning), and the one which causes rotation to the left, *laevorotatory* (left-turning). Optically active substances are of two kinds, those which are optically active only in the solid state, such as quartz, and those which are optically active when molten or in solution as well as when crystalline, *e.g.*, glucose, fructose, etc. In the latter type of substances optical activity is inherent in the molecular structure rather than in the crystalline firm.

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*It is a naturally occurring form of calcium carbonate, $CaCO_3$.

It has been found that only a small proportion of organic compounds are optically active. Each optically active compound is found to exist in two forms which differ in the direction in which they rotate polarized light. These forms are called *optical isomers*. These are distinguished by prefixing their names by d- and l- for dextrorotatory and laevorotatory respectively, *e.g.*, d-lactic acid and l-lactic acid.

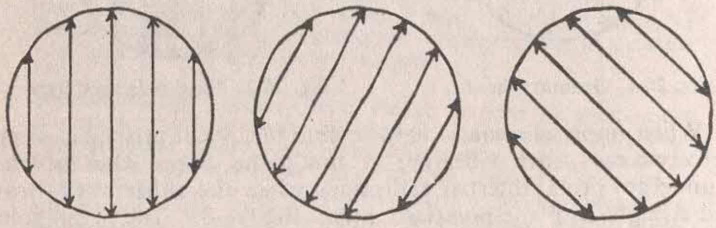


Fig. 26-4. (*a*) Plane polarized right (*b*) Plane rotated to right (dextrorotatory) (*c*) Plane rotated to left (laevorotatory).

## 3. Use of Polarimeter

The apparatus used for measuring the rotation of plane polarized light by an optically active compound is called a polarimeter. It consists of a removable glass tube, called sample tube placed between two Nicol prisms as shown in Fig. 26-5. The prism at the left end is fixed; it is called the *polarizer*. The prism at the right end or eyepiece, is rotatable and joined to a wheel which is marked off in degrees; it is called the *analyzer*. The polarizer and analyzer transmit plane-polarized light in one direction. So, a maximum amount of light will reach the observer when the polarizer and analyzer are

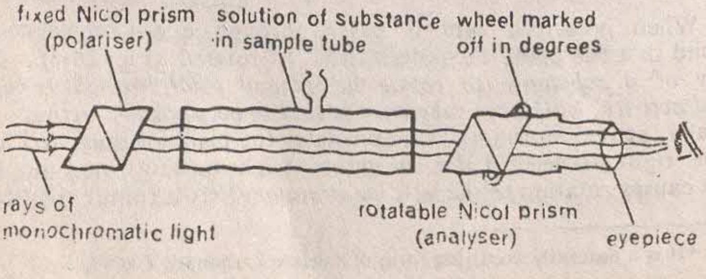


Fig. 26-5. The polarimeter.

aligned and passing light vibrating in the same plane. When using the polarimeter, the polarizer is turned until minimum light is observed in the eyepiece. This is the zero point for the instrument and the value is read from the scale. In this position the axes of the two prisms are exactly at right angles so that none of the polarized light coming through the polarizer is transmitted through the analyzer.

The sample tube is filled with a solution of a known concentration of the substance under investigation. If the substance is optically inactive, no effect is observed. If, however, the substance is optically active, a deflection of the polarized light occurs. As a result, a certain amount of light will pass through the analyzer to the observer. The analyzer a now rotated to the new position of maximum darkness. The number of degrees (α) through which the analyzer has been turned is equal to the degrees through which the polarized light is rotated by the solution. If the polarizer is turned in a clockwise direction. the substance is dextrorotatory; if the polarizer is turned in an anticlockwise direction, the substance is laevorotatory. The working of the polarimeter is schematically depicted in Fig. 26-6.

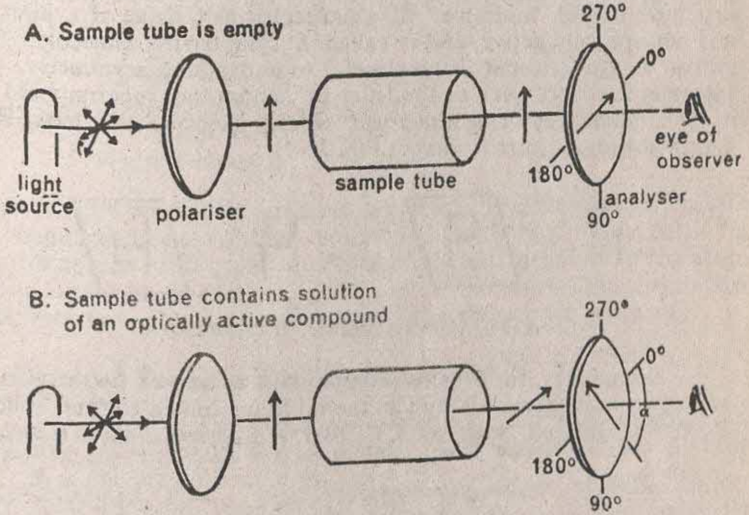


Fig. 26-6. Schematic working of a polarimeter.

For any given solute the rotation depends on the length and concentration of solution, the wavelength of the light, and the temperature. These factors are accounted for in the term *specific rotation* which is defined as the number of degress of rotation produced in the plane of polarized light passing through a tube 1 decimeter in length, filled with a solution containing 1 gram of the solute in 1 cubic centimetre of solution at a specified temperature.

Such a concentrated solution cannot be obtained for most substances. Hence, the specific rotation is calculated by the formula

$$[\alpha]_D^t = \frac{\alpha}{l.c}$$

where, $[\alpha]_D^t$ = the specific rotation at a temperature $t$, using monochromatic light of wavelength $D$ (usually light from a sodium lamp),

$\alpha$ = the measured rotation, expressed in degrees,

$l$ = the length of tube containing the solution in decimetres, and

$c$ = concentration in grams per ml of solution.

It is conventional to regard $[\alpha]_D^t$ as positive for dextrorotatory substances and negative for laevorotatory substances.

## 4. Asymmetric Carbon Atom and Enantiomorphs

Optical activity arises from the lack of symmetry in the structure of the molecule. If a molecule has a plane of symmetry, it is not optically active, and is called a symmetrric molecule. The mirror image concept is very useful to understand asymmetry. An asymmetric object, such as the letter P, cannot be superimposed on its mirror image; a symmetrical object, such as the letter H, is identical with its mirror image (Fig. 26-7).

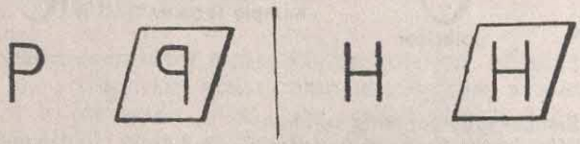


Fig. 26-7. P is asymmetric; H is symmetric

Asymmetry in organic compounds is caused by the presence of one or more carbon atoms in the molecule linked to four different atoms or groups, such as CHClBrI. *A carbon atom in a molecule*

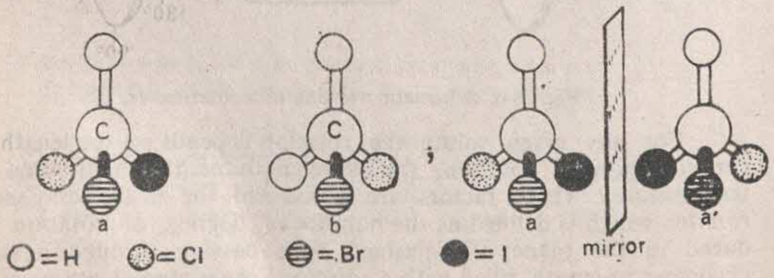
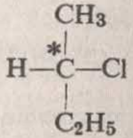


Fig. 26-8. (left) Two forms (*a* and *b*) of CHClBr; (right) *a* and its non-superimposable mirror image *a'* which is identical with *b*.

*with four different atoms or groups attached to its four valencies is called an asymmetric carbon atom.* Such a grouping permits of two different arrangements in space, leading to the existence of optical isomers. For example, the compound CHClBrI can exist in two forms *a* and *b* shown in Fig. 26-8 which differ in the spatial arrangement of the atoms H, Cl, Br, and I. The two forms are related to each other as an object and its non-superimposable mirror image That is, neither of the two forms is superimposable on its mirror image.

The two forms of a molecule which are mirror image of each other or opposites are called **enantiomorphs** (Gr. *enantios*, opposite, and *morphe*, form). Two examples of enantiomorphs, each containing one asymmetric carbon atom (marked with asterics) are given below :

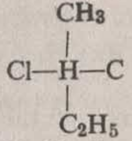
1.



$$\begin{array}{c}\mathrm{CH_3}\\ {}^{*}|\\ \mathrm{H-C-Cl}\\ |\\ \mathrm{C_2H_5}\end{array}$$

d-2-chlorobutane

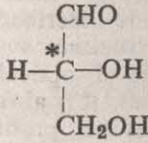
and



$$\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{Cl-H-C}\\ |\\ \mathrm{C_2H_5}\end{array}$$

*l*-2-chlorobutane

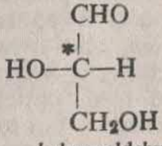
2.



$$\begin{array}{c}\mathrm{CHO}\\ {}^{*}|\\ \mathrm{H-C-OH}\\ |\\ \mathrm{CH_2OH}\end{array}$$

d-glyceraldehyde

and



$$\begin{array}{c}\mathrm{CHO}\\ {}^{*}|\\ \mathrm{HO-C-H}\\ |\\ \mathrm{CH_2OH}\end{array}$$

*l*-glyceraldehyde

It must be clearly understood that the structural formulae of the enantiomorphs of each compound are actually identical. The enantiomorphs differ only in the spatial configurations of the atoms which cannot be shown in 2-dimensional structural formulae; otherwise, they have the same atoms linked together in the same way.

## 5. Optical Isomers of Lactic Acid

Lactic acid is one of the simplest compounds exhibiting optical isomerism. It contains one asymmetric carbon atom in the molecule $CH_3.\overset{*}{C}H(OH).COOH$. The spatial arrangement of the various groups around the asymmetric carbon atom in the molecule can occur in two ways shown in the tetrahedral formulae and projection formulae in Fig. 26-9. The two molecules with these arrangements are not superimposable, and are related to each other like an object and its mirror image. The arrangement on the left hand represents dextrorotatory, also indicated as (+) lactic acid, and that on the right hand represents laevorotatory, also indicated as (−), lactic acid.

A third form of lactic acid also exists, which does not rotate the plane of polarized light. This optically inactive form consists of

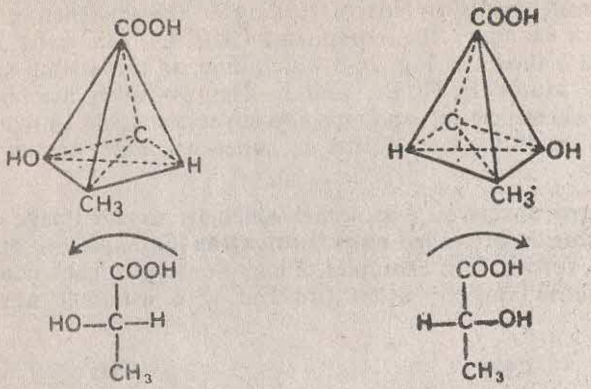


Fig. 26-9 Optical iscmers of lactic acid, $CH_3.CH(OH).COOH$.

equal amounts of the dextro- and laevo- forms combined together. It has a net rotatory power of zero since the effects of the dextro and laevo forms upon polarized light compensate each other. Thus, the d-l compound is optically inactive by what is described as *external compensation*, and is called a *racemate* or *racemic compound* (*L. racemus*, cluster). When a compound capable of optical isomerism is prepared from optically inactive substances, it is always obtained as the racemate. For example, dl-lactic acid is the product obtained from sour milk or in the following reactions :

$$(1)\ \underset{\text{acetaldehyde}}{CH_3CHO} \xrightarrow{HCN} \underset{\text{acetaldehyde cyanohydrin}}{CH_3.CH(OH)CN} \xrightarrow[H^+]{\text{hydrolysis}} \underset{\text{dl-lactic acid}}{CH_3.CH(OH).COOH}$$

$$(2)\ \underset{\text{propionic acid}}{CH_3.CH_2.COOH} \xrightarrow{Br_2} \underset{\text{1-bromopropionic acid}}{CH_3.CHBr.COOH} \xrightarrow{HOH} \underset{\text{dl-lactic acid}}{CH_3.CH(OH)COOH}$$

Dextrorotatory lactic acid occurs naturally in muscle, and can be obtained from meat extract. It is also called sarcolactic acid, (Greek *sarkos*, flesh). With muscular activity, glycogen present in muscles breaks down to give sarcolatic acid, the accumulation of which in the muscles causes fatigue. During rest, the accumulated sarcolatic acid is slowly reconverted into glycogen.

Laevorotatory lactic acid is formed in the fermentation of sucrose by *Bacillus acidi laevolactiti*.

## 6. Optical Isomers of Tartaric Acid

The tartaric acids, $COOH.\overset{*}{C}H(OH).\overset{*}{C}H(OH).COOH$, present the classic example of optically active compounds having two similar asymmetric carbon atoms, each one linked to the same four different groups, *viz.*, H, OH, COOH, and $-CH(OH)COOH$. There are three possible spatial arrangements of the various groups in the molecule, shown by means of projection formulae in Fig. 26-10.

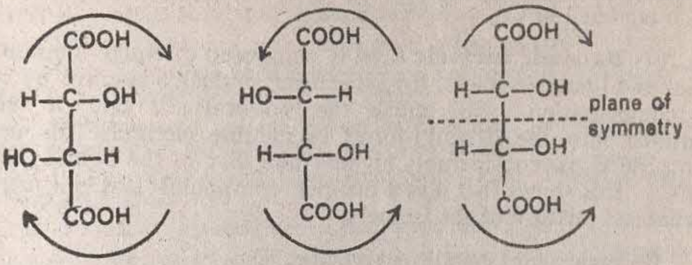


Fig. 26-10. Projection formulae of the optical isomers of tartaric acid, CH(OH).COOH—CH(OH)COOH.

These configurations correspond respectively to the dextrorotatory tartaric acid, laevorotatory tartaric acid, and mesotartaric acid which is optically inactive due to a plane of symmetry. Note that the d- and l-forms of tartaric acid are mirror images of each other. Thus, the various isomers of tartaric acid are :

(1) **Dextro-tartaric acid** in which the two halves of the molecule are both dextrorotatory, and reinforce one another in their effect. Therefore, the molecule as a whole is dextrorotatory.

Tartaric acid from natural sources, such as grapes and tamarind, is dextrorotatory.

(2) **Laevo-tartaric acid** in which the two halves of the molecules are both laeovorotatory, and strengthen the effect of each other on polarized light.

Laevo-tartaric acid does not occur in nature and is obtained from racemic tartaric acid by removing its dextro constituent with an optically active base.*

Both the dextro and laevo forms of tartaric acid have the crystal form of prisms, which melt at 170°C.

(3) **Meso-tartaric acid** is optically inactive since one half of the molecule has a dextrorotatory configuration and the other half a laevorotatory configuration. Thus, the two parts of the molecule have equal but opposite effect on polarized light, and the molecule as a whole has a rotatory power of zero. It may also be noted that the upper half of the molecule is a mirror image of the lower half. Hence, mesotartaric acid is optically inactive by what is termed *internal compensation*.

Mesotartaric acid does not occur in nature. It is formed, along with racemic tartaric acid, when the dextro or laevo acid is

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*Such a process of isolating optically active isomers from a racemic compound is called *resolution*.

heated with water at 170°C in a sealed tube. It forms rhombic crystals which melt at 140°C.

(4) **Racemic tartaric acid** is composed of equal amounts of the d- and l-tartaric acids. It is, therefore, optically inactive by external compensation. So, unlike the mesotartaric acid, it can be separated into the d- and l-forms by suitable methods. Its melting point, 206°C is considerably higher than that of the d- and l-forms, 170°C. This shows that it is a distinct compound and not merely a mechanical mixture of the isomers.

Racemic acid crystallizes in plates.

## 7. Properties of Enatiomorphs

The physical and chemical properties of enatiomorphs, *i.e.*, optical isomers, are alike. However, such substances usually differ markedly in their physiological effect.

**1. Physical properties.** Enantiomorphs (*i.e.*, the d- and l-isomers) have identical physical properties in every respect except in their effect on polarized light, which they rotate by exactly equal amounts but in opposite directions. Thus their specific rotations, $[\alpha]_D$, are numerically equal. The physical properties of enantiomorphs differ significantly from those of their optically inactive isomers (Table 26-1).

**Table 26-1** *Physical properties of tartaric acids*

| *Isomers* | *M.P.* | *Density* | *Crystal form* | *specific rotation*, $[\alpha]_D^{20}$ | *Solubility, 20° g/100 g* $H_2O$ | $K_a$ |
|---|---|---|---|---|---|---|
| Dextro | 170° | 1·760 | prismatic | +12° | 139 | $9{\cdot}7\times10^{-4}$ |
| Laevo | 170° | 1·760 | prismatic | −12° | 139 | $9{\cdot}7\times10^{-4}$ |
| Racemic | 206°C | 1·788 | rhombic | 0 | 20·6 | $9{\cdot}7\times10^{-4}$ |
| Meso | 140°C | 1·666 | plates | 0 | 125 | $6{\cdot}0\times10^{-4}$ |

**2. Chemical properties.** Optically active isomers show identical chemical behaviour, and form similar derivatives. For example, the ordinary chemical reactions of d-tartaric acid are the same as those of l-tartaric acid, and both acids form salts, esters, etc., in the same manner.

**3. Physiological effects.** Enantiomorphs differ markedly in their phsiological activity and effects. The dextro form of a compound may be fermented by a bacteria which has no effect on its laevo isomer, or vice versa. *L*-thyroxine (the active principle secreted by the thyroid gland) has several times the physiological activity possessed by its dextro isomer. D-ascorbic acid (vitamin D) is medicinally more efficient than l-ascorbic acid. Very often, living systems have only one enantiomorph of a pair. Blood sugar is d-glucose, or (+) glucose, and the amino acids obtained from the hydrolysis of proteins are laevorotatory.

## Questions

1. Explain the following terms : (*a*) optical isomerism, (*b*) polarized light, (*c*) asymmetric carbon atom, and (*d*) enantiomorphs.

2. What are dextrorotatory and laevorotatory substances ?

3. Describe the use of a polarimeter in measuring the rotation of plane polarized light by an optically active compound.

4. Give an account of the isomers of lactic acid, drawing the projection formulae as well as the tetrahedral formulae of each isomer.

5. (*a*) Describe the optical isomers of tartaric acid. Draw the projection formula of each isomer.

(*b*) Distinguish between racemic isomer and meso isomer.

6. (*a*) State with reason if the following statement is true ; if false, rewrite correctly :

'A compound with the formula R—CH(OH)—COOH can exist in two optically active forms, if R is an alkyl or aryl group.

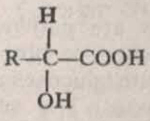
(*b*) Explain the term 'optical activity' with one example.

7. Write a brief note on the properties of enantiomorphs.

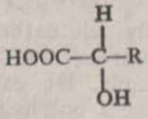
## Key

5. (*b*) Both racemic and meso isomers are optically inactive, though due to different causes. A racemic compound is optically inactive as it consists of equal quantities of d- and l- isomers which compensate each other's rotation of the plane of polarized light (external compensation). A meso isomer is optically inactive as the dextro effect of one half of the molecule is compensated by the laevo effect of the other one half (internal compensation). Since, a racemic isomer consists of both d- and l- isomers, it can be resolved into the d- and l- isomers. Meso isomer cannot be similarly resolved into the d- and l- forms.

6. (*a*) The statement is true because if R is an alkyl or aryl group, the carbon atom joined to R, H, OH, and COOH will become asymmetric and can have two different configurations related to each other as an object and its mirror image.



$$\mathrm{R{-}\overset{\overset{\large H}{|}}{\underset{\underset{\large OH}{|}}{C}}{-}COOH}$$



$$\mathrm{HOOC{-}\overset{\overset{\large H}{|}}{\underset{\underset{\large OH}{|}}{C}}{-}R}$$

# 27

# Carbohydrates

Carbohydrates are compounds of carbon, hydrogen, and oxygen, so named because their general formula $C_xH_{2y}O_y$ corresponds technically to a hydrate of carbon' $C_x(H_2O)_y$. However, the carbohydrates are not hydrates of carbon, nor all compounds which fit the general formula $C_x(H_2O)_y$ are carbohydrates, *e.g.*, formadehylde ($CH_2O$), acetic acid ($C_2H_4O_2$), and lactic acid ($C_3H_6O_3$). Furthermore, there are many carbohydrates which do not conform to the formula $C_x(H_2O_y)$, *e.g.*, rhamnose, $C_6H_{12}O_5$. However, this name has been retained even though it is not descriptive of the nature of these substances.

Among the typical carbohydrates are the sugars, starches, and cellulose. They are widely distributed in plants which form them from carbon dioxide and water by photosynthesis. The carbohydrates play an exceedingly important role in man's life. Sugars and starches are vital foodstuffs, and serve chiefly as a source of energy. Cellulose from wood or cotton provides the raw materials for making paper and textiles. The fermentation of carbohydrates gives us many useful substances, such as ethyl alcohol, butyl alcohol, acetone, lactic acid, etc.

## 1. Classification of Carbohydrates

Structurally, all carbohydrates are *polyhydroxy aldehydes or ketones*, or substances that yield either or both of these on hydrolysis. For example, the carbohydrate glucose is a polyhydroxyaldehyde and fructose a polyhydroxyketone. The carbohydrate sucrose contains neither an aldehyde nor a ketone group but gives glucose and fructose upon hydrolysis. The carbohydrates are classified into three main groups : (1) the monosaccharides, (2) the disaccharides, and (3) the polysaccharides.

**1-1. The monosaccharides.** These are the basic units of the carbohydrates and cannot be hydrolyzed further, *e.g.*, glucose, fructose, etc. The most important monosaccharides are those which contain five or six carbon atoms in their molecules, and these are practically the only monosaccharides which occur naturally. The monosaccharides with five carbon atoms are called *pentoses* and those with six carbon atoms *hexoses*. The suffix *aldo-* is used with these names if the monosaccharide contains an aldehyde group and the suffix *keto-* if it contain a ketonic group. Thus glucose is an *aldohexose* and fructose a *ketohexose*.

1-2. **The disaccharides**. These are the carbohydrates which yield two monosaccharide units on hydrolysis, *e.g.*, sucrose, maltose, etc. When hydrolyzed, each molecule of sucrose gives one molecule of glucose and one molecule of fructose while each molecule of maltose gives two molecules of glucose.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}{}^*$$

$$\underset{\text{maltose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{glucose}}{2C_6H_{12}O_6}$$

1-3. **The polysaccharides**. These are high-molecular-weight substances which yield a large number of monosaccharide units on hydrolysis. The most widely distributed polysaccharides have the general formula $(C_6H_{10}O_5)_n$, such as the starches and cellulose. Complete hydrolysis of these carbohydrates yield glucose only.

$$\underset{\text{starch or cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \rightarrow \underset{\text{glucose}}{nC_6H_{12}O_6}$$

1-4. **General properties**. The mono- and disaccharides are colourless, crystalline substances, soluble in water, and sweet in taste. They are known collectively as sugars and their names end in *-ose* : glucose, fructose, sucrose, etc The polysaccharides are non-crystalline and tasteless substances. They show poor solubility in water but can be obtained in the form of colloidal dispersions. They have unrelated names such as starch, dextrin, and inulin (exception, cellulose).

## 2. Glucose, Grape Sugar, Dextrose, $C_6H_{12}O_6$

Glucose is the most important of the monosaccharides. It is widely distributed in nature, occurring in the free state in the sap of plants fruit juices, and honey. Ripe grapes often contain up to 30 per cent of glucose (hence the name **grape sugar**). It is present in blood to the extent of about 0·1 per cent and is one of the few substances which can be injected directly into the blood stream. The work of muscles depends chiefly on the energy released in the oxidation of glucose.

2-1. **Laboratory preparation**. Glucose can be prepared in the laboratory by heating cane sugar (sucrose) with dilute hydrochloric (or sulphuric acid) for about half an hour.

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Excess of alcohol is added in which fructose dissolves; glucose is gradually deposited as crystals.

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*Sucrose and maltose are isomeric substances and so are glucose and fructose.

**2-2. Manufacture**. Glucose is prepared commercially by heating starch with water containing a small amount of acid under pressure. The changes indicated below occur :

$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} \xrightarrow[\text{heat}]{H^+,H_2O} \text{Dextrins} \xrightarrow[\text{heat}]{H^+,H_2O} \underset{\text{maltose}}{C_{12}H_{22}O_{11}} \xrightarrow[\text{heat}]{H^+,H_2O} \underset{\text{glucose}}{C_6H_{12}O_6}$$

Or, in a simplified manner,

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{H^+,\text{ heat}} nC_6H_{12}O_6$$

Often, the hydrolysis of starch is not carried to completion, and a syrup consisting of glucose, maltose, and dextrins is produced for the candy industry.

**2-3. Physical properties.** (1) Glucose crystallizes from warm solutions as colourless, anhydrous crystals, m.p. 146°C, and from cold solutions as the monohydrate, m.p. 118—120°C.

(2) It is readily soluble in water, but only slightly soluble in alcohol.

(3) It has a sweet taste (the name is, in fact, derived from the Greek word *gleukos*, meaning sweet), but is somewhat less sweet than ordinary cane sugar.

(4) In solution, glucose rotates the plane of polarized light to the right or in a *dextro* manner, and is therefore also called *dextrose*.

**2-4. Reactions**. Glucose is a polyhydroxy aldehyde, and gives the reactions of both alcohols and aldehydes. Its more important reactions are :

1. *Dehydration*. When heated strongly glucose chars, the carbon remains while the hydrogen-oxygen content is expelled as steam. When glucose is warmed with concentrated sulphuric acid, dehydration occurs very vigorously and a black mass of sugar carbon is formed.

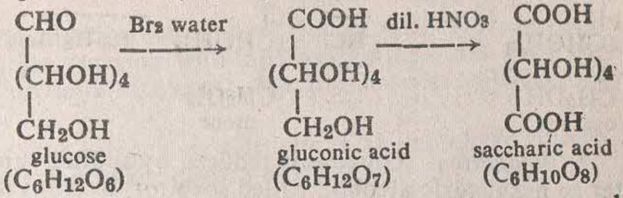
$$C_6H_{12}O_6 \rightarrow 6C + 6H_2O$$

2. *Acetylation*. When glucose is heated with an excess of acetic anhydride in the presence of anhydrous zinc chloride as catalyst, glucose penta-acetate is formed. This shows the presence of five alcoholic groups in the glucose molecule.

$$\underset{\text{glucose}}{C_6H_7O(OH)_5} + \underset{\text{acetic anhydride}}{5(CH_3.CO)_2O} \rightarrow \underset{\text{glucose pena-acetate}}{C_6H_7O(O.COCH_3)_5} + \underset{\text{acetic acid}}{5CH_3.COOH}$$

3. *Oxidation*. Glucose is a strong reducing agent. It reduces an ammoniacal solution of silver oxide (Tollen's reagent) to a silver mirror and Fehling's solution to a red precipitate of cuprous oxide on boiling. These reactions establish the presence of an aldehyde

group in the glucose molecule. The aldehyde group is converted to carboxyl group in these reactions producing gluconic acid. The same product results when glucose is oxidized with bromine water. Oxidation is gluconic acid or of glucose directly, with dilute nitric acid produced saccharic acid by the conversion of the primary alcohol group to a carboxyl group.



$$\begin{array}{ccccc} CHO & & COOH & & COOH \\ | & \xrightarrow{Br_2\ \text{water}} & | & \xrightarrow{\text{dil. } HNO_3} & | \\ (CHOH)_4 & & (CHOH)_4 & & (CHOH)_4 \\ | & & | & & | \\ CH_2OH & & CH_2OH & & COOH \\ \text{glucose} & & \text{gluconic acid} & & \text{saccharic acid} \\ (C_6H_{12}O_6) & & (C_6H_{12}O_7) & & (C_6H_{10}O_8) \end{array}$$

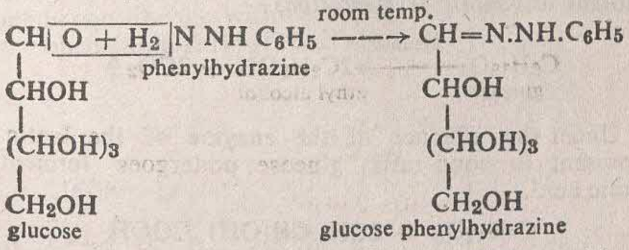
4. *With hydrogen cyanide.* Glucose forms glucose cyanohydrin by the addition of the hydrogen cyanide to its aldehyde group.

$$\underset{\text{glucose}}{C_5H_{11}O_5.CHO} + HCN \rightarrow \underset{\text{glucose cyanohydrin}}{C_5H_{11}O_5\ CH(OH)CN}$$

5. *With hydroxylamine.* Glucose behaves like a typical aldehyde in condensing with hydroxylamine to form the oxime.

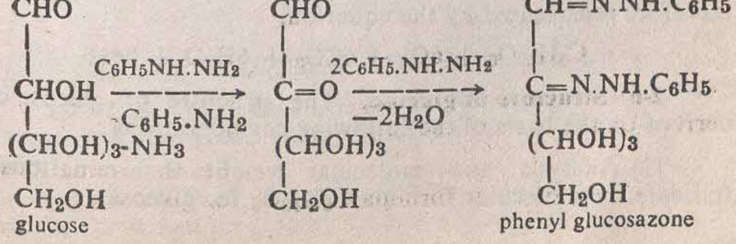
$$\underset{\text{glucose}}{C_5H_{11}O_5.CH}\boxed{O + H_2}\underset{\text{hydroxylamine}}{NOH} \rightarrow \underset{\text{glucose-oxime}}{C_5H_{11}O_5.\ CH{=}NOH} + H_2O$$

6. *With phenylhydrazine* (*a*) At room temperature one molecule of glucose condenses with one molecule of phenylhydrzine to form glucose phenylhydrazine which remains in solution.



$$\begin{array}{lcl} CH\boxed{O + H_2}\underset{\text{phenylhydrazine}}{N\ NH\ C_6H_5} & \xrightarrow{\text{room temp.}} & CH{=}N.NH.C_6H_5 \\ | & & | \\ CHOH & & CHOH \\ | & & | \\ (CHOH)_3 & & (CHOH)_3 \\ | & & | \\ CH_2OH & & CH_2OH \\ \text{glucose} & & \text{glucose phenylhydrazine} \end{array}$$

(*b*) When glucose is warmed to 100°C with excess of phenylhydrazine, a diphenylhydrazine, called glucosazone, is formed as a yellow precipitate In this reaction, one molecule of phenylhydrazine is first used up in oxidizing one CHOH group to C=0, being itself reducted to aniline and ammonia ; two molecules of phenylhydrazine then react with the CHO and C=0 groups to give the osazone.



$$\begin{array}{lclcl} CHO & & CHO & & CH{=}N\ NH.C_6H_5 \\ | & & | & & | \\ CHOH & \xrightarrow[-C_6H_5.NH_2]{C_6H_5NH.NH_2} & C{=}O & \xrightarrow[-2H_2O]{2C_6H_5.NH.NH_2} & C{=}N.NH.C_6H_5 \\ | & & | & & | \\ (CHOH)_3\text{-}NH_3 & & (CHOH)_3 & & (CHOH)_3 \\ | & & | & & | \\ CH_2OH & & CH_2OH & & CH_2OH \\ \text{glucose} & & & & \text{phenyl glucosazone} \end{array}$$

**2-2. Manufacture.** Glucose is prepared commercially by heating starch with water containing a small amount of acid under pressure. The changes indicated below occur :

$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} \xrightarrow[\text{heat}]{H^+,H_2O} \text{Dextrins} \xrightarrow[\text{heat}]{H^+,H_2O} \underset{\text{maltose}}{C_{12}H_{22}O_{11}} \xrightarrow[\text{heat}]{H^+,H_2O} \underset{\text{glucose}}{C_6H_{12}O_6}$$

Or, in a simplified manner,

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{H^+,\text{ heat}} nC_6H_{12}O_6$$

Often, the hydrolysis of starch is not carried to completion, and a syrup consisting of glucose, maltose, and dextrins is produced for the candy industry.

**2-3. Physical properties.** (1) Glucose crystallizes from warm solutions as colourless, anhydrous crystals, m.p. 146°C, and from cold solutions as the monohydrate, m.p. 118—120°C.

(2) It is readily soluble in water, but only slightly soluble in alcohol.

(3) It has a sweet taste (the name is, in fact, derived from the Greek word *gleukos*, meaning sweet), but is somewhat less sweet than ordinary cane sugar.

(4) In solution, glucose rotates the plane of polarized light to the right or in a *dextro* manner, and is therefore also called *dextrose*.

**2-4. Reactions.** Glucose is a polyhydroxy aldehyde, and gives the reactions of both alcohols and aldehydes. Its more important reactions are :

1. *Dehydration.* When heated strongly glucose chars, the carbon remains while the hydrogen-oxygen content is expelled as steam. When glucose is warmed with concentrated sulphuric acid, dehydration occurs very vigorously and a black mass of sugar carbon is formed.

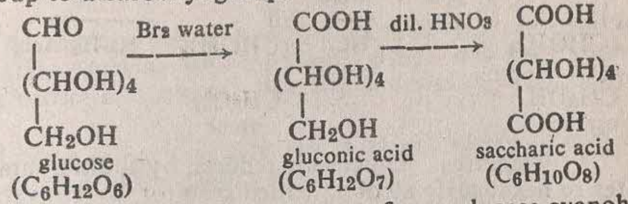
$$C_6H_{12}O_6 \rightarrow 6C + 6H_2O$$

2. *Acetylation.* When glucose is heated with an excess of acetic anhydride in the presence of anhydrous zinc chloride as catalyst, glucose penta-acetate is formed. This shows the presence of five alcoholic groups in the glucose molecule.

$$\underset{\text{glucose}}{C_6H_7O(OH)_5} + \underset{\text{acetic anhydride}}{5(CH_3.CO)_2O} \rightarrow \underset{\text{glucose pena-acetate}}{C_6H_7O(O.COCH_3)_5} + \underset{\text{acetic acid}}{5CH_3.COOH}$$

3. *Oxidation.* Glucose is a strong reducing agent. It reduces an ammoniacal solution of silver oxide (Tollen's reagent) to a silver mirror and Fehling's solution to a red precipitate of cuprous oxide on boiling. These reactions establish the presence of an aldehyde

group in the glucose molecule. The aldehyde group is converted to carboxyl group in these reactions producing gluconic acid. The same product results when glucose is oxidized with bromine water. Oxidation is gluconic acid or of glucose directly, with dilute nitric acid produced saccharic acid by the conversion of the primary alcohol group to a carboxyl group.



$$\begin{array}{c}CHO\\|\\(CHOH)_4\\|\\CH_2OH\\\text{glucose}\\(C_6H_{12}O_6)\end{array}\xrightarrow{Br_2\ \text{water}}\begin{array}{c}COOH\\|\\(CHOH)_4\\|\\CH_2OH\\\text{gluconic acid}\\(C_6H_{12}O_7)\end{array}\xrightarrow{\text{dil. }HNO_3}\begin{array}{c}COOH\\|\\(CHOH)_4\\|\\COOH\\\text{saccharic acid}\\(C_6H_{10}O_8)\end{array}$$

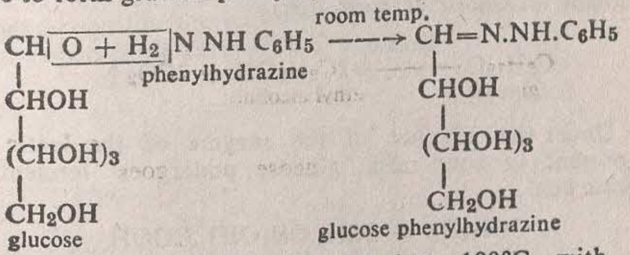
4. *With hydrogen cyanide.* Glucose forms glucose cyanohydrin by the addition of the hydrogen cyanide to its aldehyde group.

$$\underset{\text{glucose}}{C_5H_{11}O_5.CHO} + HCN \rightarrow \underset{\text{glucose cyanohydrin}}{C_5H_{11}O_5\ CH(OH)CN}$$

5. *With hydroxylamine.* Glucose behaves like a typical aldehyde in condensing with hydroxylamine to form the oxime.

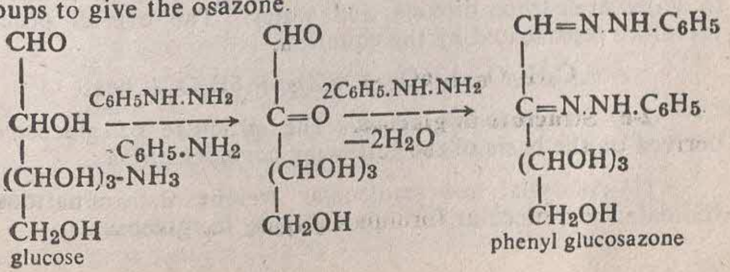
$$\underset{\text{glucose}}{C_5H_{11}O_5.CH}\boxed{O + H_2}\underset{\text{hydroxylamine}}{NOH} \rightarrow \underset{\text{glucose-oxime}}{C_5H_{11}O_5.\ CH{=}NOH + H_2O}$$

6. *With phenylhydrazine* (*a*) At room temperature one molecule of glucose condenses with one molecule of phenylhydrzine to form glucose phenylhydrazine which remains in solution.



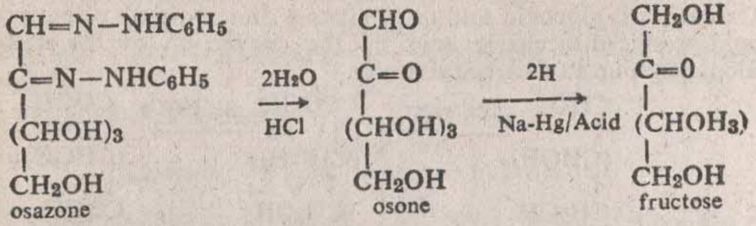
$$\begin{array}{l}CH\boxed{O + H_2}N\ NH\ C_6H_5\\|\qquad\qquad \text{phenylhydrazine}\\CHOH\\|\\(CHOH)_3\\|\\CH_2OH\\\text{glucose}\end{array}\xrightarrow{\text{room temp.}}\begin{array}{l}CH{=}N.NH.C_6H_5\\|\\CHOH\\|\\(CHOH)_3\\|\\CH_2OH\\\text{glucose phenylhydrazine}\end{array}$$

(*b*) When glucose is warmed to 100°C with excess of phenylhydrazine, a diphenylhydrazine, called glucosazone, is formed as a yellow precipitate In this reaction, one molecule of phenylhydrazine is first used up in oxidizing one CHOH group to C=0, being itself reducted to aniline and ammonia ; two molecules of phenylhydrazine then react with the CHO and C=0 groups to give the osazone.



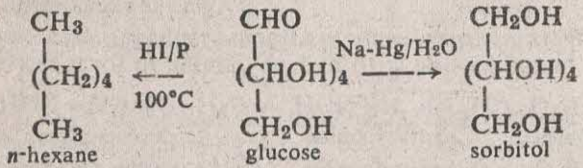
$$\begin{array}{l}CHO\\|\\CHOH\\|\\(CHOH)_3\\|\\CH_2OH\\\text{glucose}\end{array}\xrightarrow[-C_6H_5.NH_2\ -NH_3]{C_6H_5NH.NH_2}\begin{array}{l}CHO\\|\\C{=}O\\|\\(CHOH)_3\\|\\CH_2OH\end{array}\xrightarrow[-2H_2O]{2C_6H_5.NH.NH_2}\begin{array}{l}CH{=}N\ NH.C_6H_5\\|\\C{=}N.NH.C_6H_5\\|\\(CHOH)_3\\|\\CH_2OH\\\text{phenyl glucosazone}\end{array}$$

**Conversion of glucose into fructose.** This is achieved in the following steps : (1) Conversion of glucose into osazone (2) hydrolysis of osazone to osone, and (3) reduction of osone.



$$\begin{array}{l} \mathrm{CH{=}N{-}NHC_6H_5} \\ | \\ \mathrm{C{=}N{-}NHC_6H_5} \\ | \\ \mathrm{(CHOH)_3} \\ | \\ \mathrm{CH_2OH} \\ \text{osazone} \end{array} \xrightarrow[\mathrm{HCl}]{\mathrm{2H_2O}} \begin{array}{l} \mathrm{CHO} \\ | \\ \mathrm{C{=}O} \\ | \\ \mathrm{(CHOH)_3} \\ | \\ \mathrm{CH_2OH} \\ \text{osone} \end{array} \xrightarrow[\text{Na-Hg/Acid}]{\mathrm{2H}} \begin{array}{l} \mathrm{CH_2OH} \\ | \\ \mathrm{C{=}0} \\ | \\ \mathrm{(CHOH_3)} \\ | \\ \mathrm{CH_2OH} \\ \text{fructose} \end{array}$$

7. *Reduction.* Glucose is reduced by sodium amalgam and water to hexahydric alcohol, called sorbitol, by conversion of the aldehyde group ($-CHO$) to the primary alcohol group ($-CH_2OH$). Complete reduction, by heating with concentrated hydriodic acid red phosphorus, yields *n*-hexane.



$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{(CH_2)_4} \\ | \\ \mathrm{CH_3} \\ n\text{-hexane} \end{array} \xleftarrow[100^\circ\mathrm{C}]{\mathrm{HI/P}} \begin{array}{l} \mathrm{CHO} \\ | \\ \mathrm{(CHOH)_4} \\ | \\ \mathrm{CH_2OH} \\ \text{glucose} \end{array} \xrightarrow{\mathrm{Na\text{-}Hg/H_2O}} \begin{array}{l} \mathrm{CH_2OH} \\ | \\ \mathrm{(CHOH)_4} \\ | \\ \mathrm{CH_2OH} \\ \text{sorbitol} \end{array}$$

8. *Fermentation.* (*a*) A solution of glucose is fermented by the enzyme zymase, present in yeast, producing ethyl alcohol and carbon dioxide (*alcoholic fermentation*).

$$\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow{\text{zymase}} \underset{\text{ethyl alcohol}}{2C_2H_5OH} + 2CO_2 \uparrow$$

(*b*) Under the influence of the enzyme of the lactic acid bacteria present in sour milk, glucose undergoes fermentation giving lactic acid.

$$\underset{\text{glucose}}{C_6H_{12}O_6} \rightarrow \underset{\text{lactic acid}}{2CH_3.CH(OH).COOH}$$

**2·5. Glucose as a nutrient.** Glucose is a valuable nutrient. The carbohydrates we eat are converted into glucose in the digestive tract ; the glucose is then carried by the blood to all the tissues of the body. The energy required for muscular work is released primarily by the consecutive oxidation of glucose, the end products to which are carbon dioxide and water. The overall process is therefore represented by the equation.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{heat}$$

**2-6. Structure of glucose.** The structure of glucose can be derived on the basis of the following considerations :

(1) Analysis and molecular weight determinations data indicate the molecular formula $C_6H_{12}O_6$ for glucose.

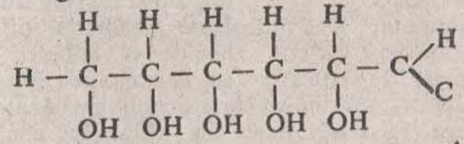
(2) The reduction of glucose to *n*-hexane shows that is has six carbon atoms linked in an unbranched chain.

(3) The formation of the penta-acetate shows that there are five hydroxyl groups in the glucose molecule. The molecule can be stable only if each hydroxyl group is linked to a different carbon atom.

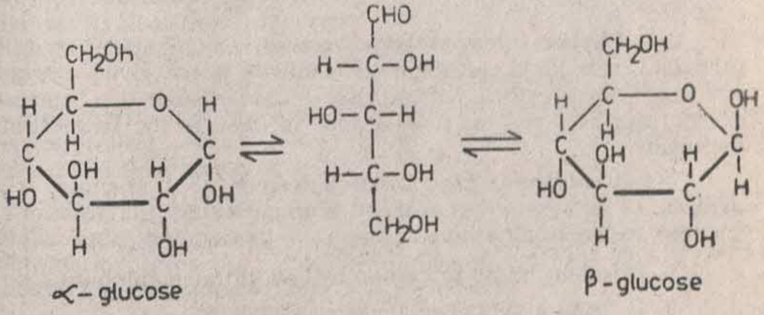
(4) The addition reaction of glucose with hydrogen cyanide, its condensation reaction with hydroxylamine, and the reducing action of glucose all indicate the presence of a-CHO group in glucose.

On obvious valency considerations, the aldehyde group can only be at the end of the carbon chain.

On the basis of all these facts, the following structure is attributed to the glucose molecule.



X-ray analysis of glucose reveals, however, that it has a six-membered ring structure in the crystals. This accounts for the existence of two cyclic isomers, α glucose and β glucose which differ in the number of hydrogen atoms on one side of the plane of the ring. In a solution of glucose both of these isomers are in dynamic equilibrium with each other and with a small proportion of the open-chain form (Fig. 27-1).



α- glucose

β - glucose

Fig. 2-71. The equilibrium forms of glucose in solution.

**2-7. Uses.** (1) *As a foodstuff.* As it is easily absorbed, glucose supplies needed energy quickly without taxing the digestive system.

(2) *In medical practice*, for the interavenous feeding of patients for whom feeding by mouth is inadvisable .

(3) *In the confectionery industry*, in making candied fruit jelly, jams, caramel, treacle-cakes, etc.

(4) *In the textile industry*, in the finishing of fabrics.

(5) *As a reducing agent*, in making silver mirrors and tinsel.

## 3. Fructose, Levulose, $C_6H_{12}O_6$

Fructose, also called levulose and fruit sugar, occurs in fruit juices and in honey. Chemically combined with glucose in the disaccharide known as sucrose, it occurs in sugar cane and sugar beets.

**3-1. Laboratory preparation**. Fructose can be prepared in the laboratory by warming cane sugar with dilute sulphuric acid, whereby the cane sugar is hydrolyzed into glucose and fructose. The product is strongly cooled and treated with slaked lime. A fructosate of composition $C_6H_{12}O_6.CaO$ is precipitated leaving the more soluble glucosate in solution. The precipitate is filtered off, washed, and suspended in water. Carbon dioxide is bubbled through the suspension, causing the fructosate to decompose into fructose and calcium carbonate. The insoluble calcium carbonate is removed and the fructose recovered from the filtrate by concentration and crystallization.

$$\underset{\text{fructosate}}{C_6H_{12}O_6.CaO} + CO_2 \rightarrow CaCO_3\downarrow + \underset{\text{fructose}}{C_6H_{12}O_6}$$

**3-2. Manufacture**. Fructose is prepared commercially by the hydrolysis of inulin, $(C_6H_{10}O_5)_n$, a polysaccharide closely related to starch, and found in dahlia bulbs and artichokes, with dilute sulphuric acid.

$$\underset{\text{inulin}}{(C_6H_{10}O_5)_n} + nH_{12}O \xrightarrow{H^+} \underset{\text{fructose}}{nC_6H_{12}O_6}$$

**3-3. Physical properties**. Fructose is a colourless, crystalline substance, m.p. 95°C. It dissolves readily in water giving a solution which is laevorotatory. It is also soluble in alcohol. Fructose is nearly twice as sweet as sucrose and, in fact, is the sweetest of all the sugars.

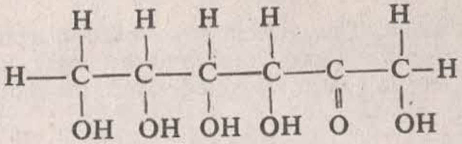
**3-4. Reactions**. Except the difference that fructose is not oxidized to a carboxylic acid by bromine water, the reactions of fructose are essentially similar to those of its isomer glucose. Thus—

1. It is dehydrated to carbon by concentrated sulphuric acid.
2. It forms a penta-acetate when acetylated.
3. It reduces Fehling's solution and Tollen's reagent.
4. It forms a cyanohydrin with hydrogen cyanide.
5. It forms an oxime with hydroxylamine.
6. When heated with excess of phenylhydrazine it forms phenylfructosazone, which is identical with phenylglucosazone.

7. It is reduced to sorbitol by sodium amalgam and water.

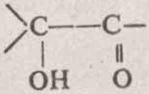
8. It is fermented to ethyl alcohol by the enzyme zymase in yeast.

3-5. **Structure**. The open chain-form of fructose has the structure.



$$\mathrm{H-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{O}{\overset{}{C}}-\underset{OH}{\overset{H}{C}}-H}$$

The reducing properties of fructose are attributed to the hydroxy ketogroup :



Like glucose, fructose also exists in the cyclic isomeric forms, α and β fructose. In solution, these forms are in dynamic equilibrium with each other and with the open-chain form.

## 4. Sucrose, Cane Sugar, $C_{12}H_{22}O_{11}$

Sucrose is the most important of all disaccharides, and is the ordinary sugar we know so well. It occurs to the extent of about 15 per cent in sugar cane and sugar beet which are its principle sources. It is also contained in much smaller amounts in the sap of the birch and the maple, and in carrots, melons, etc.

4-1. **Production of sucrose.** Sucrose is one of the purest chemical substances that nature provides, and its production merely involves its isolation from sugar cane or beets. The production of sugar from sugar cane or sugar beet involves the following operations.

*1. Extraction of juice.* The cane is shredded and crushed between rollers. The crushed material is moistened with water for a second and third extraction.

Sugar is extracted from beets by reducing them to thin shreds mechanically and placing the shreds in water. The sugar passes into the water by diffusion. This operation is carried out in large tanks, called diffusors, which are connected in series.

*2. Treatment with milk of lime.* The extracted juice is treated with milk of lime to neutralize the organic acids and coagulate the proteins. The sucrose, however, remains in solution since it forms a soluble saccharate with the calcium hydroxide. The coagulated mass is removed by filtration.

*3. Treatment with carbon dioxide.* The solution is treated with carbon dioxide which precipitates the excess of lime as calcium carbonate. The preciptate of calcium carbonate adsorbs and carries down most suspended impurities.

4. *Concentration of the juice.* The clear juice is concentrated in closed vessels under reduced pressure to prevent the decomposition and charring of sugar.

5. *Crystallization.* The concentrated solution containing only 6 to 8 per cent water is run into a tank and the sugar is allowed to crystallize. The crystals are separated from the mother liquor by centrifuging.

6. *Refining.* The crude sugar is dissolved in water and refined by treatment with lime and carbon dioxide much in the same way as the raw juice was processed. The solution is decolorized with animal charcoal before the final crystallization. Refined sugar is 99·98 per cent pure.

Cane sugar and beet sugar are identical when carefully purified.

In the extraction of sucrose from sugar canes, the residual mother liquor is a dark syrupy liquid known as molasses. It contains 55 to 70 per cent of sugars by weight, mostly the uncrystallizable glucose and fructose. It is used to make treacle, or mixed with cattle feed, or is fermented to alcohol.

**4-2. Physical properties.** (1) Sucrose is a white, crystalline compound, m.p. about 160°C. The molten sucrose solidifies into an amorphous, transparent mass called *caramel.*

(2) Excepting, fructose, it is the sweetest of all sugars.

(3) It is freely soluble in water, and dissolves in about one-third of its weight of water at room temperature. It is almost insoluble in alcohol.

(4) It is dextrorotatory.

**4-3. Reactions.** The important reactions of sucrose can be described under the following headings :

*1. Dehydration.* When heated above its melting point, sucrose loses water forming a brown substance, caramel, used for colouring and flavouring rum, vinegar, and many foodstuffs. Stronger heating causes charring to almost pure carbon.

When sucrose is warmed with concentrated sulphuric acid, the dehydration occurs very vigorously leaving a black swollen mass of sugar carbon.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{Conc. } H_2SO_4} 12C + 11H_2O$$

*2. Hydrolysis.* When sucrose is boiled with a dilute mineral acid, or acted upon by the enzyme invertase (yeast) in solution, it is hydrolysed to an equimolecular mixture of glucose and fructose.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+ \text{ or invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Sucrose is dextrorotatory and so is glucose, but fructose is even more strongly laevorotatory. Consequently, as the hydrolysis progresses, the original dextro rotation decreases, reaches zero, and finally changes to the laevo direction. This phenomenon of the reversal of the direction of rotation is called *inversion* of cane sugar, and the resulting mixture of glucose and fructose is known as the *invert sugar.* This mixture occurs extensively in honey.

3. *Oxidation.* When warmed with concentrated nitric acid, sucrose is oxidized to oxalic acid.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + 9O_2 \rightarrow \underset{\text{oxalic acid}}{6(COOH)_2} + 5H_2O$$

However, sucrose is not a reducing sugar and has no effect upon Tollen's reagent or Fehling's solution.

4. *Acetylation.* When boiled with acetic anhydride and fused sodium acetate, sucrose yields an octa-acetyl derivative. This shows that sucrose molecule contains eight free OH groups.

5. *Formation of sucrosates.* When a concentrated solution of sucrose is treated with calcium hydroxide or strontium hydroxide, a precipitate of the corresponding sucrosate is formed, *e.g.*, $C_{12}H_{22}O_{11}.2SrO$, etc.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + 3Ca(OH)_2 \rightarrow \underset{\text{calcium sucrosate}}{C_{12}H_{22}O_{11}.3CaO} \downarrow + 3H_2O$$

These sucrosates decompose to give back sucrose when carbon dioxide is bubbled into their aqueous suspensions. Use is made of the formation and decomposition of sucrosates for the recovery of sucrose from molasses.

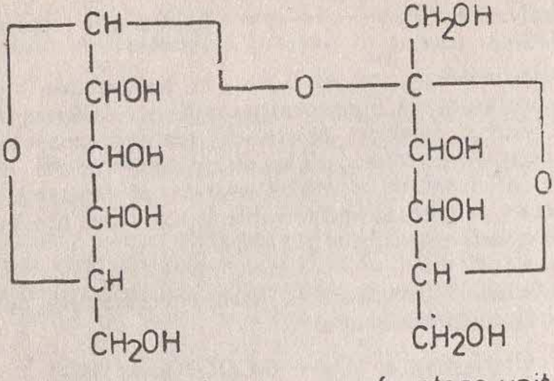
**4-4. Structure.** (1) The hydrolysis of sucrose shows that its molecule consists of a link-up of a molecule each of glucose and fructose with the loss of a water molecule.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

(2) The acetylation of sucrose indicates the presence of eight hydroxyl groups in its molecule.

(3) The absence of reducing properties and the inability of sucrose to form oxime, cyanohydrin, etc., point to the absence of a carbonyl group in the molecule.

On the basis of the above facts it is reasonable to infer that the sucrose molecule is made up of glucose and fructose molecules linked through their respective aldehyde and keto groups. Thus, the structure of sucrose can be written as :



glucose unit fructose unit

4.5. **Uses**. (1) As a sweetening agents in foodstuffs, candies, syrups, etc. Invert sugar, made from sucrose, is used in candy manufacture because of its sweetness and its property of remaining non-crystalline.

(2) As a preservative in fruit products, *e.g*, jams, jellies, etc., (fermentation does not occur at high concentrations of sucrose).

(3) For the preparation of oxalic acid.

(4) For making sucrose octa-acetate used in anhydrous adhesives, for rendering paper transparent and oil-repellant, and for denaturing alcohol.

## 5. Detection of Sugars

1. All carbohydrates produce a black mass of carbon when warmed with concentrated sulphuric acid.

2. All sugars give *Molish's test*. To dilute solution of the sugar (about 5 ml.) in a test tube is added a drop of an alcoholic solution of $\alpha$-naphthol. Concentrated sulphuric acid is then poured carefully along the side of the test tube so that it forms a separate layer at the bottom. A beautiful violet colour appears at the junction of the two liquids.

3. Glucose and fructose can be distinguished from each other by the *furfural test*. The sugar is treated with an alcoholic solution of $\alpha$-naphthol and concentrated hydrochloric acid, and the mixture is heated to boiling. An immediate violet colour is produced with fructose; the colour appears after a few minutes with glucose.

4. Sucrose is readily distinguished from both glucose and fructose because it does not produce a silver mirror with Tollen's reagent nor does it reduce Fehling's solution. A positive test is to

boil it with dilute sulphuric acid, neutralize, and add Fehling's solution, when a red precipitate of cuprous oxide is formed.

## 6. Starch, $(C_6H_{10}O_5)_n$

The polysaccharide starch is the reserve carbohydrate of plants. It is stored in all grains and tubers as a future food supply for the germinating seed. The principal commercial sources of starch are potatoes, rice, maize (corn), wheat, and barley.

**6-1. Production of starch.** (*a*) *From potatoes.* The potatoes are washed and then shredded mechanically. The shredded mass is washed with water in sieves. The starch granules released from the cells of the tuber pass through the sieve with the water and settle at the bottom of a vat. These are washed thoroughly, separated from the water, and dried with hot air.

(*b*) *From rice, etc.* The grains are soaked in water to soften the crust. These are then ground to break the cells and release the starch contained in them. The ground mass is washed with water, and the extract is passed over fine sieves. The starch passes out in a milky suspension. On standing, the starch granules settle down. These are washed and dried with hot air.

**6-2. Physical properties.** (1) Starch is a white powder with no taste or smell. Its melting point is not known as it is decomposed on heating.

(2) As normally prepared, starch is not soluble in cold water. In hot water, starch swells and forms a colloidal solution, behaving as a lyophillic colloid.

**6-3. Reactions.** (1) Starch does not reduce Fehling's solution or Tollen's reagent.

(2) It reacts with iodine solution, giving a deep violet colour which disappears on heating but reappears on cooling. This is an extremely sensitive test for either starch or free iodine..

(3) *Hydrolysis.* When boiled with a dilute acid, starch is hydrolysed to glucose,

$$(C_6H_{10}O_5)n + nH_2O \xrightarrow{H^+} nC_6H_{12}O_6$$

Actually, the hydrolysis occurs in stages leading to the formation of several grades of *dextrins* of progressively decreasing molecular weights. The dextrins are also represented by the formula $(C_6H_{10}O_5)_n$, but the value of *n* is variable and much smaller than in starch.

The enzyme *diastase*, present in malt and in saliva, hydrolyses starch into maltose. This is an important step in the manufacture of alcohol from starch.

**6-4. Starch as a nutrient.** Starch is the basic carbohydrate in our food. When the food is chewed, it is partially hydrolysed to glucose by the enzymes contained in the saliva. The hydrolysis of starch continues in the intestines and the glucose formed used for producing energy. Surplus glucose is stored in the liver as a polysaccharide, called *glycogen* or *liver starch*, $(C_6H_{10}O_5)n$. It readily hydrolyzes to glucose and the reserve of this material in the liver provides glucose to the blood stream as it is used up.

**6-5. Dextrins.** $(C_6H_{10}O_5)n$. These are produced by the partial hydrolysis of starch by boiling it with water under pressure at about 200°C. These are white powders and are used as glue, to thicken dyes in printing designs on fabric, and for sizing paper, etc. The conversion of starch into dextrin accounts for the lustre of starched linen, as well as the formation of the shiny crust on baked bread.

**6-6. Structure.** The structure of starch is extraordinarily complex. The complete hydrolysis of starch yields only glucose indicating that it is a polysaccharide made up of glucose units. The starch molecule consists of huge branched molecules each containing about 200 – 1000 glucose molecules linked together by oxygen atoms. Molecular weight estimates of starch by means of osmotic pressure measurements range from 17,000 to 225,000.

**6-7. Uses.** Apart from its principal use as a food, starch finds many uses in industry. These are :

1. For the production of glucose and dextrins by hydrolysis.
2. In the production of ethyl alcohol by fermentation.
3. As a stiffening agent in laundry.
4. In sizing cloth and paper.
5. In making adhesive pastes; wheat starch is particularly used for making pastes because it is very adhesive.

## 7. Cellulose, $(C_6H_{10}O_5)n$

Cellulose is a polysaccharide having the same empirical formula as starch. It is the most abundant organic substance found in nature serving as the skeletal material of plants. It is the meterial of the cell walls of plants and hence its name cellulose from the Latin *cellula*, meaning cell. Coniferous wood contains about 60 per cent cellulose and cotton more than 90 per cent. Filter paper (unsized) and absorbent cotton are almost pure cellulose.

**7-1. Production of pure cellulose.** (a) *From cotton.* The cotton is first washed with alcohol and ether to remove waxes and fats and then boiled with 1 per cent alkali to dissolve out pectin-like substances. The residual material is pure cellulose. The absorbent cotton for hospital use is made in this manner.

(*b*) *From wood.* Wood is a combination of *lignin*, which is a non-carbohydrate material, and cellulose. Lignin is removed by digesting wood chips at about 150°C with an aqueous solution containing calcium and magnesium hydrogen sulphites. The lignin dissolves leaving behind the insoluble cellulose. This method of preparing cellulose is called the sulphite process. In another method known as the sulphate process, the wood is digested with a solution of sodium hydroxide, sodium sulphide, and sulphur. Again, the lignin dissolves and the cellulose remains as the insoluble residue.

**7-2. Physical Properties.** (1) Cellulose is a white, fibrous solid possessing considerable tensile strength.

(2) It is insoluble in water and in most liquids, but dissolves in ammoniacal copper hydroxide solution (Schweitzer's reagent).

**7-3. Chemical properties.** (1) *Chemical inertness.* Cellulose is not affected by dilute acids, alkalis, and weak oxidizing agents.

(2) *Action of heat.* When heated in air, cellulose (*e.g.*, wood, cotton, paper, etc.) burns giving carbon dioxide and water. When heated out of contact with air, the cellulose undergoes thermal decomposition, giving off water and volatile organic substances such as methyl alcohol and acetic acid.

(3) *Hydrolysis.* On prolonged boiling with dilute sulphuric or hydrochloric acid, cellulose is hydrolysed through a number of intermediate stages to finally yield glucose.

$$\underset{\text{cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{H^+} \underset{\text{glucose}}{nC_6H_{12}O_6}$$

(4) *Formation of esters.* If cellulose is treated with nitric acid-sulphuric acid mixture, nitrate esters are formed : cellulose mononitrate, cellulose dinitrate, and cellulose trinitrate.

$$\underset{\text{cellulose}}{(C_6H_{10}O_5)_n} \quad \underset{\text{cellulose mononitrate}}{(C_6H_9O_4NO_3)_n} \quad \underset{\text{cellulose dinitrate}}{[C_6H_8O_3(NO_3)_2]_n} \quad \underset{\text{cellulose trinitrate}}{[C_6H_7O_2(NO_3)_3]_n}$$

This shows the presence of three free hydroxyl groups in cellulose.

When acetylated with acetic anhydride in the presence of concentrated sulphuric acid, cellulose forms the ester cellulose triacetate.

**7-4. Mercerised cellulose.** When cellulose is agitated with about 20 per cent aqueous sodium hydroxide, a number of its physical properties are changed. The resulting form of cellulose, called mercerised cellulose, is lustrous and absorbs dyes more readily than untreated cellulose.

**7-5. Cellulose as a nutrient** Cellulose has no nutritive value for man and other carnivorous animals because they lack the enzymes necessary for the hydrolysis of the polymer. The cellulose material (roughage) in the food, therefore, passes out undigested. Ruminants (cud-chewing animals, such as the cow) are able to utilize cellulose as a food with the aid of the bacteria in their intestinal tract which decompose cellulose.

**7-6. Structure of cellulose**. Like starch, cellulose is also a polymer of glucose and has the same empirical formula $(C_6H_{10}O_5)_n$. However, the molecules of starch and cellulose differ in their degree of polymerization and their structure.

The degree of polymerization of cellulose is considerably higher than that of starch, and molecular weight estimates of some samples of cellulose range from 100,000 to 500,000. The cellulose molecule is made up of about 1500 glucose residues on an average.

The cellulose and starch also differ in the structure of their molecules. The starch molecules have branched chains; the cellulose molecules have a linear structure. It is because of its linear structure that cellulose forms such fibrous materials as cotton, flax and hemp. In natural fibres the cellulose macromolecules are oriented along the axis of the fibre, Fig. 27-2 (*a*). Since the orderly arrangement gives rise to big intermolecular forces, the fibres possess great mechanical strength. The spinning of cotton, flax, etc. weaves these natural fibres into longer and stronger threads. In the cellulose of timber, the linear molecules are not oriented in one direction and have a random arrangement, Fig. 27-2 (*b* . Consequently, it is not suited for weaving threads.

Fig. 27-2. (*a*) Orderly arrangement of the linear cellulose molecules oriented along the axis of fibre in cotton, flax and hemp.

(*b*) Random arrangement of the linear cellulose molecules in timber.

**7-7. Uses.** Cellulose has very many applications :

(1) Cellulose obtained from timber is used for making paper.

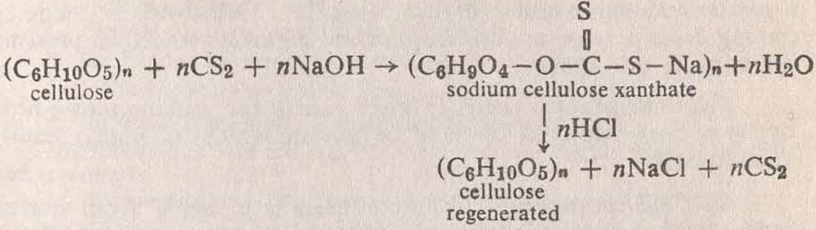
(2) Finely divided cellulose, as wood flour, when mixed with appropriate binding materials, is manufactured in a variety of useful forms such as cardboard, hardboard, and other forms of value to the building industry.

(3) Cellulose fibres from cotton, hemp, and flax are used to produce threads, textiles, and ropes.

(4) Cellulose is used in the manufacture of rayon, cellophane, 'safety' films, explosives, etc.

**7-8. Products of cellulose**. Some products of cellulose of commercial importance are described in the following paragraphs :

*1. Rayon*. This is the most important of all artificial fibres. In the commonest process, called the *viscose process*, wood pulp is treated with sodium hydroxide solution and carbon disulphide. The resulting sticky liquid contains cellulose as the soluble sodium cellulose xanthate, and is called viscose. This is sprayed through tiny openings into a bath of sulphuric acid when the cellulose is regenerated in the form of gossamer-like continuous fibres. Rayon thread is made from these fibres. The formation and decomposition of sodium cellulose xanthate can be shown by the following equations :



$$\underset{\text{cellulose}}{(C_6H_{10}O_5)_n} + nCS_2 + nNaOH \rightarrow \underset{\text{sodium cellulose xanthate}}{(C_6H_9O_4-O-\overset{\overset{S}{\|}}{C}-S-Na)_n} + nH_2O$$

$$\Big\downarrow nHCl$$

$$\underset{\substack{\text{cellulose}\\\text{regenerated}}}{(C_6H_{10}O_5)_n} + nNaCl + nCS_2$$

As a fabric rayon is light, silky, easily laundered and a good conductor of heat. Rayon finds use not only in clothing but also for making tyre cord, tufted carpets, and hose pipes.

*2. Cellophane*. If the viscose solution is extruded into the acid bath through a long fine slit, the cellulose is regenerated in the form of a thin transparent sheet called cellophane. This is treated with glycerol to increase flexibility, and used as a material for wrappings.

*3. Paper*. The cellulose used for making paper is obtained from wood, cotton rags, cereal straw, and similar materials. These are shredded and digested under pressure with calcium hydrogen sulphite. This dissolves the lignin and leaves the cellulose as wood pulp. The pulp is washed with water and bleached white with chlorine or sulphur dioxide. It is then run over screens that catch and mat the fibres into a continuous sheet as the water drains off. The sheet is dried by passing it over heated rollers.

Many substance, such as rosin, aluminium sulphate, clay, barium sulphate, dyes, etc., are added to the pulp to produce paper of special properties. For example, rosin or glue is used as sizing to fill up the spaces between the cellulose fibres; this gives the paper a smooth finish and prevents ink from spreading on it. Glazed papers contain aluminium sulphate or clay, and waxed paper is impregnated with paraffin.

*4. Cellulose nitrates*. When cellulose is treated with a mixture of concentrated nitric acid and sulphuric acid below 40°, nitrate esters are formed. The product is commonly called *nitrocellulose*, but is misnamed; it is not a nitroderivative but a nitrate ester of the OH groups. The degree of nitration in the product is determined by the percentage of nitrogen in a sample of it. A completely nitrated cellulose contains three nitro groups per glucose unit with a nitrogen content of about 14 per cent.

The cellulose nitrates containing about 13 per cent nitrogen are explosives and are known as **gun cotton**. They are used in the preparation of **smokeless powders** which, upon explosion, give off only the colourless gases nitrogen, hydrogen, carbon monoxide, carbon dioxide, and steam, and no smoke. The 'double base' powders are mixtures of gun cotton and nitroglycerine.

The products of lower nitration are soluble in a mixture of ethyl alcohol and ether, and are called *pyroxylin*. These are used as a plastic material in quick drying lacquers **Celluloid** is made by mixing dried pyroxylin with camphor and pigments, and then pressing the mixture into sheets or blocks.

Cellulose nitrates were formerly used for making movie film, but have been displaced by cellulose acetate which is not so readily inflammable.

*5. Cellulose acetate.* Cellulose acetate is made from cotton linters by the action of acetic anhydride in the presence of sulphuric acid as catalyst. The esterification of cellulose proceeds to the triacetate stage. When the reaction is complete, water is added to decompose the triacetate into the diacetate. This material is used for making non-inflammable photographic and cinema films, non-shatterable glass (safety glass), lacquers and varnishes, and as a moulding plastic for various objects. When it is dissolved in acetone and forced through fine opening into a current of warm air, the acetone evaporates leaving cellulose acetate as fine threads. This is *acetate rayon* or *Celanese*.

Acetate rayon is expensive, but superior to viscose rayon in several respects. It makes warmer garments and shrinks much less when washed. It is softer and creases little.

## Questions

**1. (*a*) What is the description of carbohydrates from a structural point of view ?**

**(*b*) Describe, with suitable examples, the classification of carbohydrates.**

**2. (*a*) How is glucose prepared in the laboratory ?**

**(*b*) How is glucose manufactured from starch ?**

**(*c*) How would you show that—**

**(*i*) glucose molecule contains 5 OH groups ?**

**(*ii*) glucose molecule contains an aldehyde group ? (Give any two reactions).**

**(*d*) Explain the use of glucose as a nutrient.**

**3. (*a*) Discuss the structure of glucose.**

**(*b*) List the important uses of glucose.**

**4. (*a*) How is fructose prepared in the laboratory ?**

**(*b*) How is fructose made on a large scale ?**

**(*c*) In what chemical reaction does fructose differ from glucose ?**

**(*d*) Write down the open chain structure of glucose and point out the part of the structure to which the reducing properties of fructose are attributed.**

5. How could the following conversions be affected :

(*a*) glucose into fructose, and

(*b*) fructose into glucose.

6. (*a*) Describe the isolation of cane sugar from sugarcane or beet. How is the product refined ?

(*b*) What happens when sucrose is

(*i*) heated alone, (*ii*) heated with conc. $H_2SO_4$,
(*iii*) boiled with dil. $H_2SO_4$, (*iv*) heated with conc. $HNO_3$,
(*v*) boiled with acetic anhydride and sodium acetate ?

(*c*) How is sugar recovered from molasses ?

7. (*a*) Discuss the structure of sucrose.

(*b*) Give the main uses of sucrose.

8. (*a*) What is Molisch's test for carbohydrates ?

(*b*) What test would you apply in order to distinguish between glucose and fructose ?

(*c*) How would you distinguish sucrose from glucose and fructose.

9. (*a*) How is starch produced from potatoes ? From rice ?

(*b*) Describe the hydrolysis of starch ?

(*c*) Explain the use of starch as a nutrient.

(*d*) What are dextrins ?

(*e*) Give the main uses of starch.

10. (*a*) How is pure cellulose obtained from cotton ? From wood ?

(*b*) Describe the hydrolysis of cellulose.

(*c*) How would you prove the presence of three free hydroxyl groups in cellulose ?

(*d*) Why does cellulose have no nutritive value ?

(*e*) List the uses of cellulose.

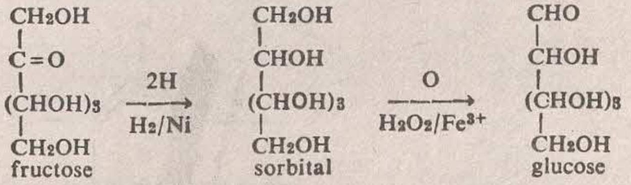
11. Describe the production of any two of the following products :

(*i*) rayon. (*ii*) paper
(*iii*) cellulose nitrates, (*iv*) cellulose acetate.

## Key

5. (*a*) see Sec. 2·4, reaction 6, page 102.

(*b*) Fructose can be converted into Glucose in the following steps : (1) reduction of fructose with hydrogen in the presence of nickel catalyst to produce the hexahydric alcohol Sorbitol, (2) oxidation of Sorbitol with $H_2O_2$ in the presence of ferric sulphate (Fenton's reagent).



$$\begin{array}{ccccc} CH_2OH & & CH_2OH & & CHO \\ | & & | & & | \\ C=O & & CHOH & & CHOH \\ | & & | & & | \\ (CHOH)_3 & \xrightarrow[H_2/Ni]{2H} & (CHOH)_3 & \xrightarrow[H_2O_2/Fe^{3+}]{O} & (CHOH)_3 \\ | & & | & & | \\ CH_2OH & & CH_2OH & & CH_2OH \\ \text{fructose} & & \text{sorbital} & & \text{glucose} \end{array}$$

28

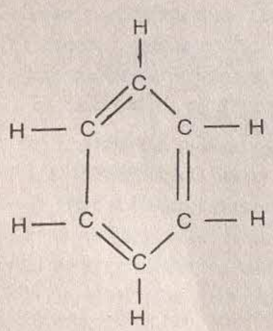
# Benzene and Chlorobenzene

There is an important class of hydrocarbons that is basically different from the various classes of hydrocarbons so far studied—the alkanes, alkenes, or alkynes. This class is the *aromatic hydrocarbons* or *arenes*. The distinctive structural features of the arenes or aromatic hydrocarbons are : (1) a much higher ratio of carbon to hydrogen than in any other class of hydrocarbons, and (2) a cyclic arrangement of six carbon atoms. These features are responsible for the distinctive chemical properties of the arenes.

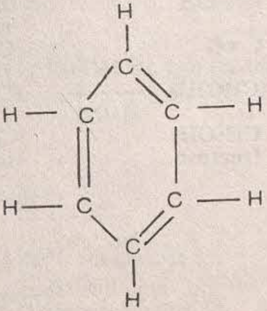
The general formula of the simple arenes which contain only one six-carbon ring, called the *benzene ring*, in the molecule is $C_nH_{2n-6}$. The first and the simplest member of this series has the molecular formula $C_6H_6$. Its name is benzene (so named because it can be obtained from benzoic acid which occurs in the naturally occurring substance *gum benzoin*). The next member of the series is toluene, $C_7H_8$, or $C_6H_5.CH_3$.

## 1. The Molecular Structure of Benzene

The molecular formula of benzene, from the analytical data, is $C_6H_6$. Modern methods of investigations have established that the six carbon atoms in the benzene molecule, each one attached to a hydrogen atom, are situated at the corners of a regular hexagon with 120° angles between each pair of bonds formed by a given hydrogen atom, and the angle between any two bonds formed by a carbon atom is 120°. In keeping with these facts and the tetravalency of carbon, the following two structures are possible for the benzene ring.



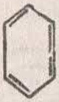
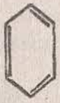
and



(I)

(II)

Measurements by electron diffraction techniques have, however, shown all carbon-carbon bonds in benzene to be identical, with bond length midway between the C—C and C=C bond lengths. Benzene is therefore regarded as a *resonance hybrid* of the above two structures. For simplicity, however, either of these structures is used to represent benzene. In a further simplification, the symbols C and H are omitted and the benzene molecule represented by any one of the following diagrams :


or,

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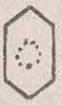
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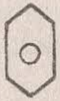


Whichever of these representations is used, it must be remembered that any of the six carbon-carbon bonds in the benzene is the same as any other and has properties unlike those of either a single bond or a double bond. In the condensed rings, both the carbon and the hydrogen atoms are understood to be located at each of the six corners.

**1-1. Delocalization of electrons in benzene.** The facts that (1) the benzene ring is planar and highly symmetrical, (2) the six carbon-carbon bonds are identical, and (3) the C—C—C bond angles are all 120°, suggest that the carbon atoms in the benzene ring are in a state of $sp^2$ hybridization. Each carbon atom, therefore, has three $sp^2$ hybrid orbitals and one pure $p$ orbital. The three $sp^2$ hybrid orbitals are used in forming three sigma bonds, two with the neighbouring carbon atoms by $sp^2$-$sp^2$ overlapping of orbitals and one with a hydrogen atom by $sp^2$-$s$ overlapping of orbitals (Fig. 28-1). Each carbon atom is then left with one unhybridized $p$ orbital (Fig. 28-2).

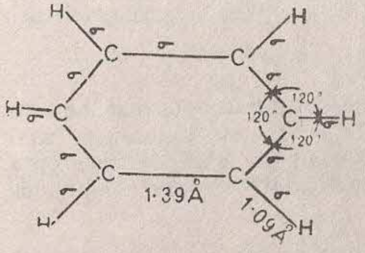


Fig. 28-1. Sigma bonds in the benzene molecule.

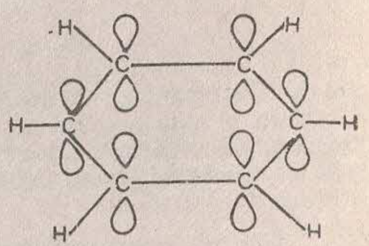


Fig. 28-2. Unhybridized $p$ orbitals on carbon atoms in the benzene ring.

The six unhybridized $2p_z$ orbitals on the carbon atoms in the ring are parallel to each other and are perpendicular to the plane of the ring. Each one of these $p_z$ orbitals can overlap to form a $\pi$ bond equally with the $p_z$ orbital on its right, or its left. Consequently all the six $p$ orbitals overlap to give a hexagonal polycentric orbital system extending above and below the plane of the $\sigma$-bonded carbon ring (Fig. 28-3). Thus, their π-electrons are not localized between the adjacent carbon atoms; they are completely delocalized, or, spread out over all the carbon atoms. The participation of π electrons in the formation of two or more bonds is called *electron deloculization*. The delocalized electrons of the carbon atoms form a doughnut shaped electron cloud above and below the plane of the ring) (Fig. 28-4).

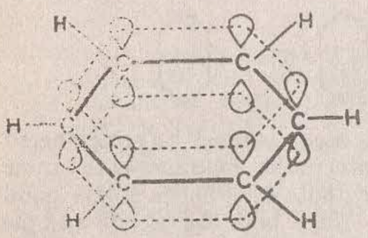


Fig. 28-3. Overlap between the $2p_z$ orbitals of the six carbon atoms in benzene ring (heavier lines indicate σ bonds between carbon atoms ; lighter ones the overlap of $2p_z$ orbitals).

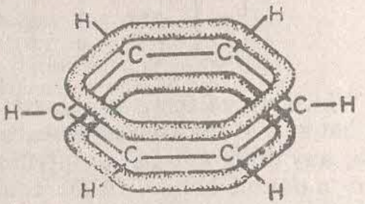
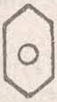
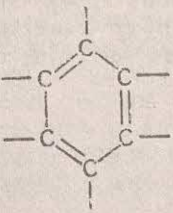


Fig. 28-4. The electron cloud of delocalized π electrons of carbon atoms in benzene ring. The circle in the graphic formula signifies electron delocalization in benzene.



## 2. Aromatic Compounds

Organic compounds containing six-carbon ring structure



are called aromatic compounds. It is interesting to note that the term 'aromatic' originally came to be used because these substances were frequently derived from natural sources having a characteristic aroma. The term, however, continues to be used for all aromatic compounds, with or without odours.

Aromatic compounds form the same classes as do the aliphatic compounds : the hydrocarbons, the halogen derivatives of hydrocarbons, hydroxy derivatives (alcohols and phenols), aldehydes, ketones, carboxylic acids and their derivatives, nitro compounds, amines, etc. However, the presence of the benzene ring profoundly influences the chemical behaviour of aromatic compounds which markedly differs from those of the aliphatic compounds of the same class.

**2-1. Sources of aromatic compounds.** The major natural source of benzene and other aromatic hydrocarbons is coal. These are not contained as such in the coal but are formed when coal is strongly heated in the absence of air to temperatures around 1000°C. The process yields coke-oven gas, *coal tar*, ammonia, water, and coke. The cool tar produced accounts for 3 to 6 per cent of the mass of the coal. It contains a large number of various aromatic hydrocarbons plus small amounts of some nitrogen and oxygen-containing organic compounds.

In recent years petroleum has become another important source of aromatic hydrocarbons. Most petroleums contain some of the aromatic hydrocarbons which can be extracted by suitable processes. In addition, the aliphatic hydrocarbons of petroleum occurring naturally and produced in the cracking process are also converted into aromatic hydrocarbons by *catalytic reforming*.

The aromatic hydrocarbons obtained from coal tar and petroleum are converted into various aromatic compounds by chemical treatment.

## 3. Benzene, $C_6H_6$

Benzene is the simplest and most important of the aromatic hydrocarbons. It is the corner stone of the entire family of aromatic compounds, and all aromatic compounds can be finally simplified to benzene.

**3-1. Laboratory preparation.** Benzene can be prepared in the laboratory by the following methods :

1. By heating sodium benzoate strongly with soda lime; the benzene vapour distils over and condenses.

$$\underset{\text{sodium benzoate}}{C_6H_5.COONa} + NaOH \xrightarrow{\Delta} \underset{\text{benzene}}{C_6H_6} \uparrow + Na_2CO_3$$

This method is analogous to the preparation of methane by the decarboxylation of sodium acetate.*

2. By passing the vapour of phenol over heated zinc turnings.

$$\underset{\text{phenol}}{C_6H_5OH} + Zn \rightarrow \underset{\text{benzene}}{C_6H_6} + ZnO$$

3. By passing acetylene under pressure through a tube heated to 400°C; the acetylene polymerizes to benzene.

$$\underset{\text{acetylene}}{3\ C_2H_2} \xrightarrow{400^\circ\ C} \underset{\text{benzene}}{C_6H_6}$$

**3-2. Manufacture.** (*a*) *From coal tar*. The coal tar is distilled into four liquid fractions. The fraction distilling over up to 170°C is called *light oil*, and contains mainly benzene, its homologues, and

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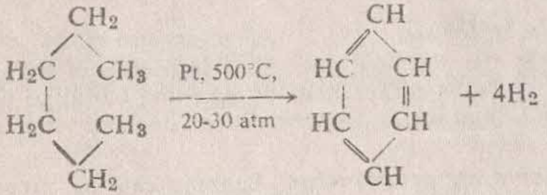
$$\underset{\text{sodium acetate}}{CH_3.COONa} + \underset{\text{(soda-lime)}}{NaOH} \xrightarrow{\Delta} \underset{\text{methane}}{CH_4} \uparrow + Na_2CO_3$$

pyridine. This fraction constitutes about 5 per cent of the weight of the coal tar.

The light oil fraction is washed successively with concentrated sulphuric acid, water, sodium hydroxide, and water. The acid removes basic substances such as pyridine; the alkali removes phenols which are acidic in nature. The washed oil is now distilled. The fraction collected up to 110° C contains 70 per cent benzene, and 30 per cent of its homologues. This fraction is carefully fractionated to separate pure benzene.

(*b*) *From petroleum.* Many aliphatic hydrocarbons are produced in the cracking of petroleum. Aliphatic hydrocarbons containing six carbon atoms in the molecule, *e.g.*, *n*-hexane, are passed under 20-30 atm pressure over platinum deposited on alumina at a temperature of about 500° C. Under these conditions the aliphatic hydrocarbon cyclises to benzene.



Probably, *n*-hexane is first dehydrogenated to the alkene before cyclisation occurs.

Benzene homologues, *e.g.*, toluene ($C_6H_5.CH_3$), are similarly produced from other aliphatic hydrocarbons obtained from petroleum.

**3-3. Physical properties.** (1) Benzene is a colourless mobile liquid with a characteristic odour.

(2) It boils at 80°C, and when cooled solidifies readily into a white crystalline mass which melts at 5.5° C.

(3) It is insoluble in and lighter than water. As such, when added to water, it forms a distinct layer above water. It is miscible with alcohol and ether in all proportions.

(4) It is a good solvent for fats, resins, sulphur, iodine, and a large number of organic compounds.

**3-4. Physiological action.** Benzene is decidedly toxic. Long exposure to benzene in low concentrations causes anaemia; continued exposure may have a fatal effect. Absorption of benzene through the skin has similar effects. Mild poisoning by benzene is marked by nausea and dizziness; acute poisoning causes death by respiratory or heart failure. However, if adequate ventilation is available, benzene can be handled safely and without any unusual precaution whatsoever.

3-5. **Reactions**. The ring of six carbon atoms in the benzene molecule is highly stable and remains intact in most chemical reactions. However, it can be saturated with hydrogen, and under sufficiently drastic conditions, may be broken by oxidation. The remarkable stability of benzene is apparent from the fact that it is not affected by dilute acids or boiling aqueous alkalis, by ordinary oxidizing or reducing agents, and does not decolorize bromine water. The hydrogen atoms in benzene can be replaced by a number of atoms and groups, such as $-Cl$, $-NO_2$, $-SO_3H$, etc.

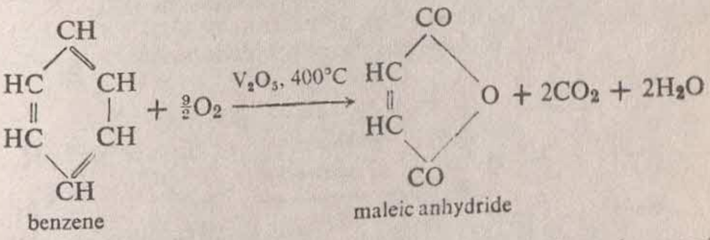
The important reactions of benzene are :

1. **Burning**. Like all hydrocarbons, benzene burns in air producing carbon dioxide and water.

$$3C_6H_6+15O_2 \rightarrow 12CO_2+6H_2O$$

The flame of burning benzene is smoky as free carbon is also produced due to its high carbon content.

2. **Oxidation**. Benzene is not attacked by chromic acid or alkaline permanganate (both powerful oxidizing agents) at room temperatures. It is only slowly oxidized by hot acidified permanganate to form oxalic and formic acids. When a mixture of benzene vapour and oxygen is passed over a vanadium pentoxide ($V_2O_5$) catalyst at 400°, the benzene is oxidized to give maleic anhydride, carbon dioxide, and water.



3. **Pyrolysis**. When benzene vapour is passed through a red hot iron tube (800°) containing a catalyst, two molecules of it unite with a loss of hydrogen molecule to form biphenyl.

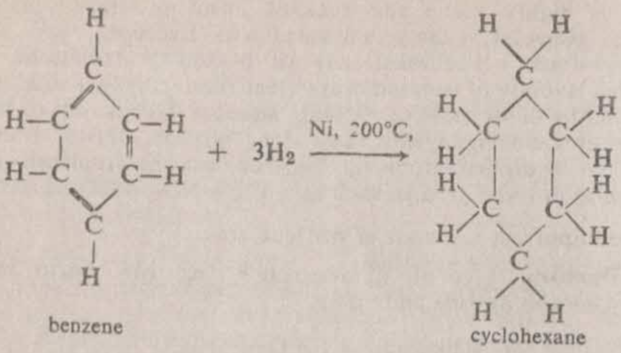
$$\underset{\text{benzene}}{2C_6H_6} \xrightarrow{800^\circ} \underset{\text{biphenyl}}{C_6H_5.C_6H_5} + H_2$$

4. **Addition reactions**. The addition reactions of benzene involve—

(*i*) *Addition of hydrogen*. Benzene adds hydrogen at about 200°C in the presence of a nickel catalyst to form cyclohexane.

$$\underset{\text{benzene}}{C_6H_6} + 3H_2 \xrightarrow{\text{Ni, } 200^\circ} \underset{\text{cyclohexane}}{C_6H_{12}}$$

Or,

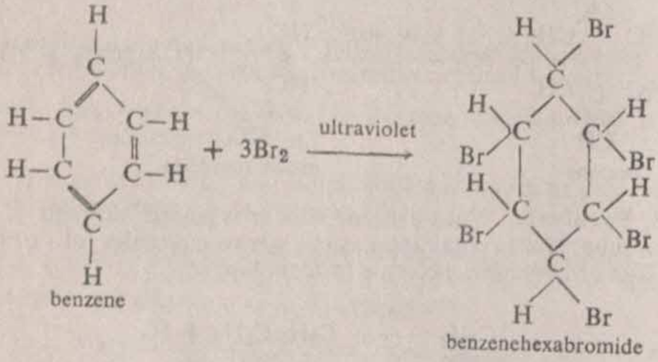


(*ii*) *Additions of halogen.* In bright sunlight (which is rich in ultraviolet light), benzene forms addition products with chlorine and bromine, forming benezenehexachloride, $C_6H_6Cl_6$, and benzenehexabromide, $C_6H_6Br_6$, respectively.

$$\underset{\text{benzene}}{C_6H_6} + 3Cl_2 \xrightarrow{\text{ultraviolet}} \underset{\text{benzenehexachloride}}{C_6H_6Cl_6}$$

$$\underset{\text{benzene}}{C_6H_6} + 3Br_2 \xrightarrow{\text{ultraviolet}} \underset{\text{benzenehexabromide}}{C_6H_6Br_6}$$

Or,



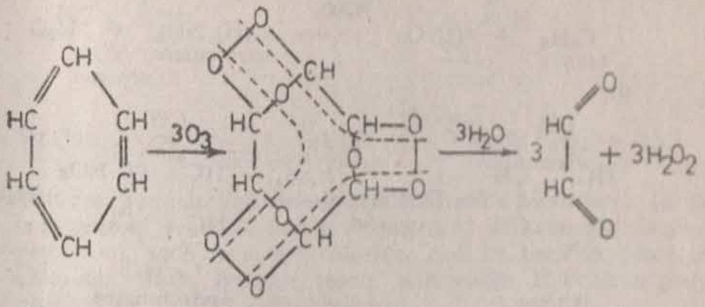
Benzenehexachloride is a white solid which exists in a number of isomeric forms. One of these is a powerful insecticide sold under the name 'Gammexane' or 'BHC'.

Iodine does not form addition products with benzene.

(*iii*) *Addition of ozone.* When ozonized oxygen is bubbled into benzene, the latter behaves as a compound containing three double bonds forming a triozonide.

$$\underset{\text{benzene}}{C_6H_6} + 3O_3 \rightarrow \underset{\text{benzene triozonide}}{C_6H_6(O_3)_3}$$

Benzene triozonide is an unstable compound, and is readily hydrolyzed to give glyoxal.

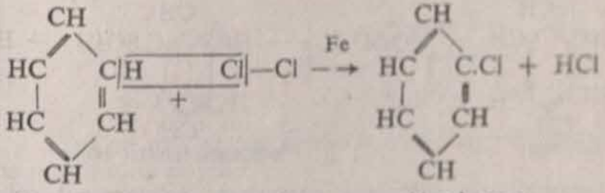


benzene benzene triozonide glyoxal (3 molecules)

**5. Substitution reactions.** In the substitution reactions of benzene, the substituent atom or group is always an electrophilic (electron-loving or electron seeking) agent. These correspond to the substitution reactions of saturated compounds. Some typical reactions are :

(*i*) *Halogenation.* When chlorine is bubbled into benzene at room temperature in diffused light in the presence of a catalyst (often called a "halogen carrier") such as iron filings, iodine, or aluminium chloride, monochlorobenzene is formed.

$$\underset{\text{benzene}}{C_6H_6} + Cl_2 \xrightarrow{Fe} \underset{\text{monochlorobenzene}}{C_6H_5Cl + HCl}$$



benzene monochlorobenzene

Prolonged chlorination, under these conditions causes further substitution, giving dichlorobenzene, $C_6H_4Cl_2$, trichlorobenzene, $C_6H_3Cl_3$, etc. Bromine also reacts with benzene under similar conditions, forming bromobenzenes, but iodine is not readily substituted into benzene in this way.

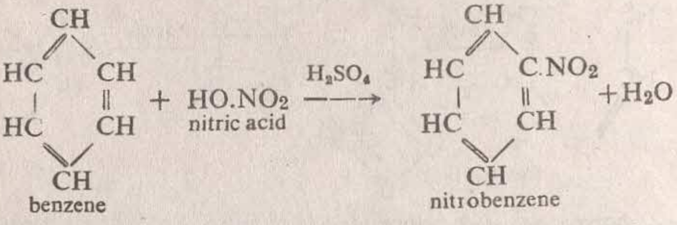
$$C_6H_6 + Br_2 \xrightarrow{Fe} HBr + C_6H_5Br \xrightarrow{+Br_2} HBr + C_6H_4Br_2, \text{ etc.}$$

Chloro- and bromobenzenes are heavy, insoluble oily substances.

(*ii*) *Nitration.* When benzene is treated with a mixture of concentrated nitric and sulphuric acids (called nitrating acid, one of its hydrogen atom is replaced by the univalent nitro-group, $-NO_2$, to form nitrobenzene.

$$\underset{\text{benzene}}{C_6H_6} + HNO_3 \xrightarrow{H_2SO_4} \underset{\text{nitrobenzene}}{C_6H_5.NO_2} + H_2O$$

or,



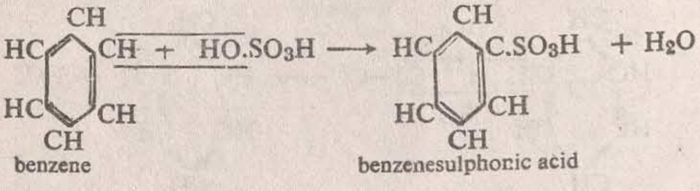
Prolonged heating with the nitrating acid gives dinitrobenzene, $C_6H_4(NO_2)_2$. Trinitrobenzene, $C_6H_3(NO_2)_3$, is eventually formed if benzene is heated with a mixture of fuming nitric acid and concentrated sulphuric acid.

It must be appreciated that nitration, unlike esterification, is not a reversible reaction. The function of sulphuric acid in the nitrating acid is not to prevent a back reaction, but to prevent dilution of nitric acid by taking up the water as it is formed.

(*iii*) *Sulphonation.* When benzene is treated with fuming sulphuric acid (oleum) at room temperature, one of the hydrogen is replaced by a sulphonic acid group, $-SO_3H$. The resulting compound is called benzenesulphonic acid.

$$\underset{\text{benzene}}{C_6H_6} + \underset{\text{(in oleum)}}{H_2SO_4} \longrightarrow \underset{\text{benzene sulphonic acid}}{C_6H_5.SO_3H} + H_2O$$

or

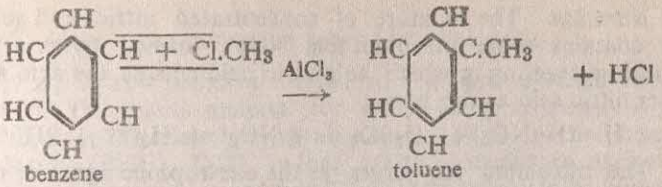


Benzenesulphonic acid is a colourless deliquescent solid, readily soluble in water, and is a strong monobasic acid. Sulphonation is therefore employed for the conversion of an insoluble aromatic hydrocarbon into a water-soluble compound.

(*iv*) *Alkylation.* When benzene is treated with an alkyl chloride in the presence of anhydrous aluminium chloride as catalyst, replacement of hydrogen atom by an alkyl group occurs forming a higher homologue of benzene.

$$\underset{\text{benzene}}{C_6H_6} + \underset{\substack{\text{methyl}\\\text{chloride}}}{CH_3Cl} \xrightarrow{AlCl_3} \underset{\substack{\text{methylbenzene}\\\text{or, toluene}}}{C_6H_5.CH_3} + HCl$$

or



Similarly, $\underset{\text{benzene}}{C_6H_6} + \underset{\text{ethyl chloride}}{C_2H_5Cl} \xrightarrow{AlCl_3} \underset{\text{ethylbenzene}}{C_6H_5.C_2H_5} + HCl$

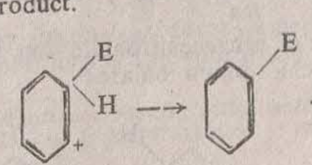
This reaction is called **Friedel and Craft's reaction**. In fact, it is a general reaction, and any compound containing a reactive halogen atom, such as acetyl chloride, can be used in place of alkyl chloride. Thus, benzene reacts with acetyl chloride to give acetophenone or phenyl[*] methyl ketone.

$$\underset{\text{benzene}}{C_6H_6} + \underset{\text{acetyl chloride}}{CH_3.COCl} \xrightarrow{AlCl_3} \underset{\substack{\text{acetophenone}\\ \text{(phenyl-methyl ketone)}}}{C_6H_5.CO.CH_3} + HCl$$

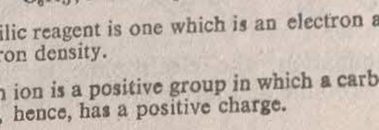
**3-6. Mechanism of substitution in the benzene ring.** The substitution in the benzene ring (*i.e.*, replacement of hydrogen) is brought about by strong oxidizing agent such as bromine or a mixture of hot concentrated sulphuric acid and nitric acid. Such reactions involve the attack of a strong electrophilic (electron-loving) reagent[**] on the benzene molecule. The mechanism of *electrophilic substitution* involves the following sequence of steps :

*i.* Generation of an electrophile, $E^+$.

*ii.* The attack of the electrophile on the benzene ring resulting in the formation of an intermediate carbonium ion[***].



*iii.* Loss of a proton by the intermediate carbonium ion to yield the substitution product.



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[*] The monovalent group of atoms obtained from benzene by the removal of one hydrogen atom, $-C_6H_5$, is called **phenyl**.

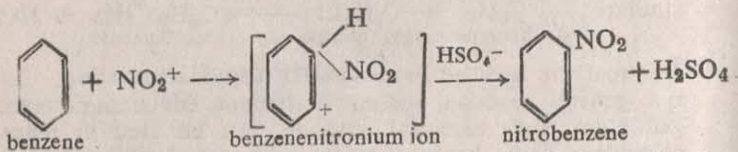
[**] An electrophilic reagent is one which is an electron acceptor and reacts at centres of high electron density.

[***] A carbonium ion is a positive group in which a carbon atom possesses a sextet of electrons, and, hence, has a positive charge.

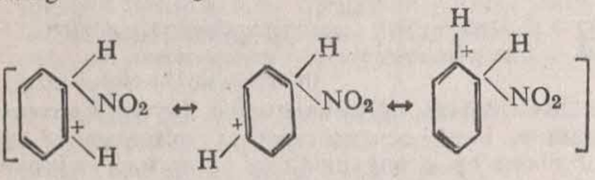
*Nitration.* The mixture of concentrated nitric and sulphuric acids contains some nitronium ion, $NO_2^+$, formed by an acid-base equilibrium reaction in which sulphuric acid acts as the acid and the weaker nitric acid as the base.

$$H-O-NO_2 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

The nitronium ion serves as the electrophilic agent or electrophile in the formation of nitrobenzene.



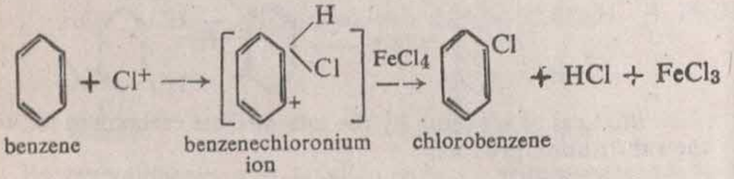
Resonance in the benzenenitronium ion may be indicated by the following contributing forms :



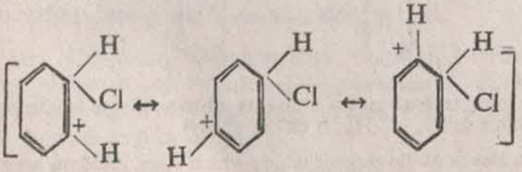
*Halogenation.* In chlorination, the electron-seeking agent is the chloronium ion, $Cl^+$, formed from ferric chloride (catalyst) and chlorine.

$$FeCl_3 + Cl_2 \longrightarrow [FeCl_4]^- + Cl^+$$

It is not necessary to postulate an existence for $Cl^+$ for any longer time than is required for it to attach itself to the ring, forming the carbonium ion. The unstable carbonium ion loses a proton, $H^+$, to form the stable bromobenzene.



As in the case of benzenenitronium ion, the contributing structures of the benzenechloronium ion are :



In bromination, the electrophile is the bromonium ion, $Br^+$, formed from bromine and ferric bromide (catalyst).

**3-7. Uses.** The important uses of benzene are :

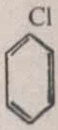
(1) *As a raw material to the vast organic chemical industry.* Benzene is the initial material for synthesizing very many organic compounds : chlorobenzene, nitrobenzene, aniline, phenol, benzene-hexachloride (BHC), DDT, nylon, dyestuffs, medicines, agricultural chemicals, detergents, monomers* for the production of high polymers, etc.

2. *As a solvent* for oils, fats, resins, rubber, sulphur, iodine, etc.

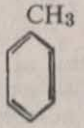
3. *As an additive to petrol.*

## 4. Derivatives of Benzene

In writing the formula of a substitution product of benzene it is conventional to show only the substituents attached to the benzene ring; the carbon and hydrogen atoms on the ring are omitted. Thus, monochlorobenzene, $C_6H_5Cl$, and toluene (methyl benzene), $C_6H_5.CH_3$, are shown as

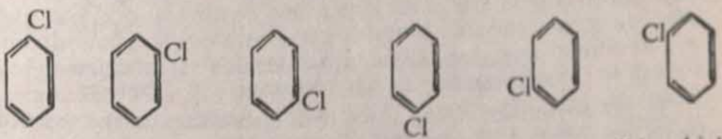


and



respectively.

(1) *Mono-derivatives.* All the six hydrogen atoms in the benzene molecule are absolutely equivalent. Therefore, *only one* monosubstituted derivative is formed, no matter which of the six hydrogen atoms of benzene is replaced. As such, all of the following formulae of chlorobenzene, $C_6H_5Cl$, are identical :



(2) *Di-derivatives.* In this case three isomers are possible which differ in the different positions of the substituent atoms in relation to

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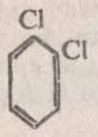
*One of the most important monomer is ethylbenzene made by Friedel and Craft's reaction (page 125). It is dehydrogenated by passing it at 600°C over a catalyst of metallic oxides.

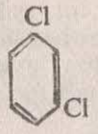
$$\underset{\text{ethylbenzene}}{C_6H_5.CH_2CH_3} \xrightarrow{600^\circ C} \underset{\text{styrene}}{C_6H_5.CH{=}CH_2} + H_2$$

The resulting compound, styrene, is polymerized into a thermoplastic, called polystyrene, $(C_6H_5.CH.CH_2)_n$. It is extensively used for electrical insulation and for making parts of refrigerators and radios, toys, and other household goods.

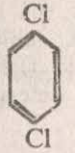
each other. Thus, there are three isomeric dichlorobenzenes, represented by the following formulae :



*ortho*dichlorobenzene
(*o*-dichlorobenzene)



*meta*dichlorobenzene
(*m*-dichlorobenzene)



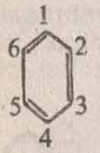
*para*dichlorobenzene
(*p*-dichlorobenzene)

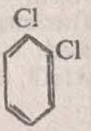
If the two substituent atoms or groups are attached to adjacent carbon atoms, the isomer is designated as *ortho* (*o*-).

If the two substituents are attached to carbon atoms in the next-but-one position (*i.e.*, separated from each other by one carbon atom), the isomer is designated *as meta* (*m*-).

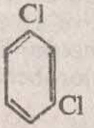
Finally, if the substituents are attached to carbon atoms separated from each other by two carbon atoms (*i.e.*, those which are diametrically opposite each other), the isomer is designated as *para* (*p*-).

These position isomers, as they are called, are often distinguished by numbering the carbon atoms in the benzene ring in a clockwise direction. The numbering begins with the carbon atom where initial substitution is assumed to have taken place. This carbon atom is numbered one. The three isomeric dichlorobenzenes are then named as follows :

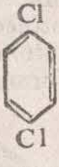




1, 2-dichlorobenzene

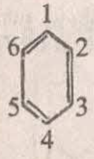


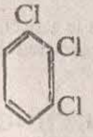
1, 3-dichlorobenzene



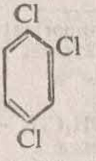
1, 4-dichlorobenzene

(3) *Tri-derivatives*. When three hydrogen atoms in the benzene molecule are replaced by identical atoms or groups, three isomers are possible. The formulae of the three isomeric trichloro-benzenes, $C_6H_3Cl_3$, are

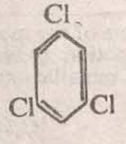




1, 2, 3-trichloro benzene



1, 2, 4-trichloro benzene

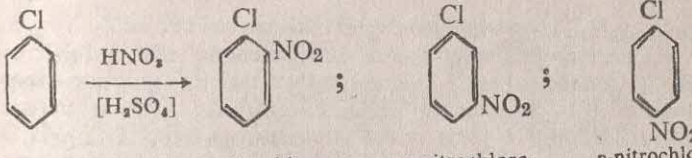


1, 3, 5-trichloro benzene

Three isomers are also possible for the tetra-substituted derivatives of benzene (with identical substituents). The penta- and hexa-substituted derivatives do not exhibit isomerism (why ?)

## 5. Orientating or Directing Effect of Groups

If chlorobenzene, $C_6H_5Cl$, is nitrated, three isomeric nitrochlorobenzenes, $C_6H_4(NO_2)Cl$, are obtained*. Two of these three isomers, the ortho and the para, are formed in relatively large quantities (29 and 70 per cent, respectively), the meta isomer is produced in negligible amounts.

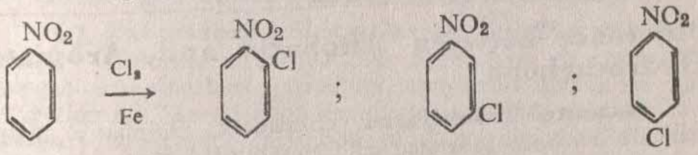


*o*-nitrochlorobenzene (about 29%)

*m*-nitrochlorobenzene (about 1%)

*p*-nitrochlorobenzene (about 70%)

On the other hand, if nitrobenzene, $C_6H_5NO_2$, is halogenated with chlorine, the *meta*nitrochlorobenzene is produced to the extent of about 93 per cent, while the amounts of the *ortho* and *para* isomers are insignificant.



*o*-nitrochlorobenzene (about 6%)

*m*-nitrochlorobenzene (about 93%)

*p*-nitrochlorobenzene (about 1%)

The obvious conclusion is that *the group already present on the benzene ring exercises some sort of directing influence upon the second entering group*. The chlorine atom directs the entering nitro group to take up *ortho* and *para* positions in preference to the *meta* position, the nitro group directs the entering chlorine atoms to take up *meta* position in preference to the *ortho* and *para* positions. A good empirical rule for predicting the directing influence of groups is that *groups containing double or triple bonds are meta-directing; others are ortho, para-directing*. Table 28-1 lists some common substituent atoms or groups according to their directive influences.

It is also significant that the ortho, para-directing groups facilitate further substitution in the benzene ring; meta-directing groups retard it. Thus, phenol ($C_6H_5OH$), aniline ($C_6H_5NH_2$), and toluene ($C_6H_5 \cdot CH_3$) readily form substitution products; nitrobenzene can be further nitrated only with difficulty.

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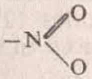
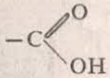
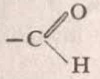
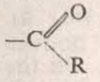
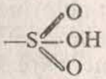
*Try drawing various possible structures to make sure that three and only three different structures can be drawn.

**Table 28-1** *Directing influence of groups*

| *Ortho, para-directing* | | *Meta-directing* | |
|---|---|---|---|
| *Name* | *formula* | *Name* | *formula* |
| Hydroxyl | $-OH$ | Nitro |  $-NO_2$ |
| Amino | $-NH_2$ | Carboxyl |  $-COOH$ |
| Alkyl | $-R$ | Aldehydic |  $-CHO$ |
| Halogens | $-Cl$<br>$-Br$<br>$-I$ | Ketonic |  $-COR$ |
| | | Sulphonic acid |  $-SO_2OH$ |

## 6. Difference between Aliphatic and Aromatic Hydrocarbons

1. **Saturated/unsaturated character.** Aliphatic hydrocarbons are of both saturated and unsaturated types ; in composition, benzene and other aromatic hydrocarbons are unsaturated. The general formula of the benzene series hydrocarbons is $C_nH_{2n-6}$ which represents a far greater degree of unsaturation than even the alkynes which have the general formula $C_nH_{2n-2}$. However, the unsaturated character of aromatic hydrocarbons is of a wholly different kind than that of aliphatic hydrocarbons, and gives rise to the so-called 'aromatic character'. It is manifested in the resistance towards the formation of addition products with hydrogen, halogens, and the halogen acids.

2. **Nitration and sulphonation**. Aromatic hydrocarbons readily undergo substitution reactions with concentrated nitric acid and sulphuric acid at quite moderate temperatures to form nitro-derivatives and sulphonic acids respectively. Aliphatic hydrocarbons, in general, do not react with these acids in a like manner.

3. **Friedel and Craft's reaction**. In the presence of anhydrous aluminium chloride, aromatic hydrocarbons react with compounds containing a reactive halogen atom, such as an alkyl chloride (RCl) or an acyl chloride (ROCl, *e.g.*, $CH_3.COCl$), to give corresponding derivatives. Aliphatic hydrocarbons do not give Friedel and Craft's reaction.

4. **Reactivity of halides**. Aliphatic halides, such as ethyl bromide, are very reactive and the halogen atom in them is readily

replaced by many other atoms and groups. The aromatic halides containing the halogen atom directly linked to the benzene ring are rather chemically inert.

5. **Oxidation**. With the exception of benzene, the aromatic hydrocarbons such as $C_6H_5.CH_3$, $C_6H_5.C_2H_5$, etc., are easily oxidized to benzoic acid. Aliphatic hydrocarbons are resistant to oxidation.

6. **The influence of the phenyl group** ($C_6H_5$). Compounds containing the phenyl group are appreciably more acidic than the corresponding aliphatic compounds. Thus (*a*) phenol, $C_6H_5OH$, is acidic; methyl alcohol, $CH_3OH$, is neutral, (*b*) benzoic acid, $C_6H_5.COOH$, is a strong acid; acetic acid, $CH_3.COOH$, is a weak acid, and (*c*) aniline, $C_6H_5.NH_2$, is far less basic than methylamine, $CH_3.NH_2$.

7. **Nature of primary amines**. Aromatic primary amines, such as aniline ($C_6H_5.NH_2$), form *diazo-compounds* with nitrous acid; aliphatic primary amines do not give diazo compounds.

## 7. Chlorobenzene, Phenyl chloride, $C_6H_5Cl$

**1-1. Laboratory preparation**. (*a*) *By direct chlorination of benzene*. Chlorine is passed into benzene in the presence of a halogen carrier such as iron filings, anhydrous aluminium chloride, or pyridine. The reaction is exothermic and cooling may be necessary to prevent formation of dichlorobenzene. Direct light must be excluded to avoid addition reactions.

$$C_6H_6 + Cl_2 \xrightarrow{Fe} C_6H_5Cl + HCl$$

When the theoretical increase in weight has occurred the product is poured into cold water and separated. It is washed first with sodium hydroxide solution and then with water, dried with anhydrous calcium chloride, and fractionally distilled.

(*b*) *By the decomposition of benzenediazonium chloride*. Benzenediazonium chloride is made by dissolving aniline in excess of hydrochloric acid, cooling the solution to 0°C, and adding sodium nitrite solution. The nitrous acid produced from sodium nitrite and hydrochloric acid reacts with aniline hydrochloride to give benzenediazonium chloride.

$$C_6H_5.NH_2 + HCl \rightarrow C_6H_5.NH_3Cl \text{ (aniline hydrochloride)}$$

$$\underset{\substack{\text{aniline}\\\text{hydrochloride}}}{C_6H_5.NH_3Cl} + HNO_2 \rightarrow \underset{\substack{\text{benzenediazonium}\\\text{hydrochloride}}}{C_6H_5.N_2Cl} + 2H_2O$$

The benzenediazonium chloride solution is slowly added to a solution of cuprous chloride in concentrated sulphuric acid contained in a flask. The mixture is then heated on boiling water bath under a reflux condenser to complete the decomposition of benzenediazonium chloride to chlorobenzene.

$$\underset{\text{benzenediazonium chloride}}{C_6H_5N_2Cl} \xrightarrow{Cu_2Cl_2} \underset{\text{chlorobenzene}}{C_6H_5Cl} + N_2\uparrow$$

The chlorobenzene formed is recovered by steam distillation as an oily liquid. It is separated from water in the distillate, dried over anhydrous calcium chloride, and then distilled using air condenser.

**1-2. Manufacture**. Chlorobenzene is made industrially by passing a mixture of benzene vapour, hydrogen chloride, and air over a catalyst of copper chloride (*Raschig process*).

$$\underset{\text{benezene}}{2C_6H_6} + 2\,HCl + \tfrac{1}{2}O_2 \xrightarrow{CuCl_2} \underset{\text{chlorobenzene}}{2C_6H_5Cl} + H_2O$$

**1-3. Physical properties.** (1) Chlorobenzene is a colourless, pleasant-smelling boiling liquid, b.p. 132°.

(2) It is heavier than and insoluble in water but is freely miscible with alcohol and ether.

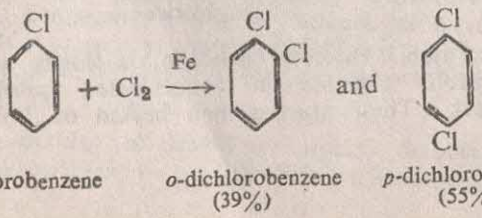
(3) It is volatile in steam.

**1-4. Reactions.** The chlorine atom in chlorobenzene is very firmly held to the benzene ring. As such, under ordinary conditions, the replacement reactions which occur readily with alkyl halides *e.g.*, ethyl chloride, do not take place with chlorobenzene. Thus, it is unaffected by boiling alkalis, aqueous or alcoholic, or by alcoholic solutions of ammonia, potassium cyanide, etc. However, under drastic conditions it is possible to replace the chlorine atom in chlorobenzene by —OH or —$NH_2$ groups.

The main reactions of chlorobenzene can be described under the following headings :

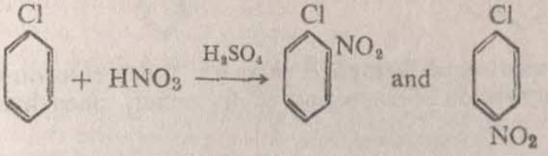
1. **Substitution on the ring**. The chlorine in chlorobenzene is *ortho*, *para*-directing. However, the rate of substitution is less than it is in benzene.

(*a*) *Chlorination*. The chlorination of chlorobenzene with iron as catalyst gives a mixture of mainly *ortho-* and *para*-dichlorobenzenes.



chlorobenzene   *o*-dichlorobenzene (39%)   *p*-dichlorobenzene (55%)

(*b*) *Nitration*. The nitration of chlorobenzene with concentrated nitric acid-sulphuric acid mixture gives mainly *ortho-* and *para-*chloronitrobenzenes.



chlorobenzene *o*-chloronitrobenzene *p*-chloronitrobenzene

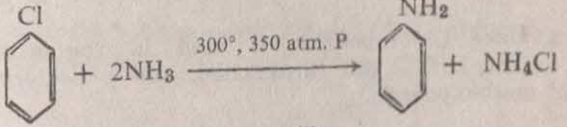
**2. Replacement of —Cl.** (*a*) *By —OH.* When chlorobenzene is heated with aqueous sodium hydroxide to 350°C and 200 atm. pressure, the chlorine is replaced by hydroxyl group to give phenol.

$$\underset{\text{chlorobenzene}}{C_6H_5Cl} + NaOH \xrightarrow{350°,\ 200\ \text{atm. P}} \underset{\text{phenol}}{C_6H_5OH} + NaCl$$

(*b*) By *—NH₂*. The chlorine in chlorobenzene can be replaced by —NH₂ group by heating it with ammonia under 350 atm pressure in the temperature ranging from 250 to 350°C. The product is aniline, $C_6H_5.NH_2$. This reaction is catalysed by cuprous oxide.

$$C_6H_5Cl + H.NH_2 \rightarrow C_6H_5.NH_2 + HCl$$
$$(HCl + NH_3) \rightarrow NH_4Cl$$

or,

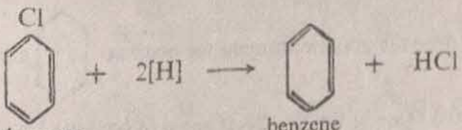


chlorobenzene aniline

**3. Reduction.** When treated with nascent hydrogen from sodium amalgam and aqueous-alkaline alcohol, chlorobenzene is reduced to benzene.

$$C_6H_5Cl + 2[H] \rightarrow C_6H_6 + HCl$$

or,

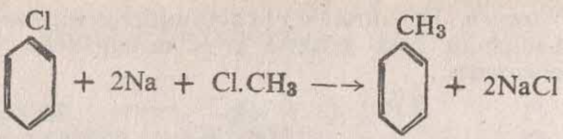


chlorobenzene benzene

**4. Wurtz-Fittig reaction.** The reaction is similar to Wurtz reaction for the synthesis of alkanes. Thus, when metallic sodium is added to a dry ethereal solution of chlorobenzene and methyl chloride, methylbenzene or toluene is formed.

$$\underset{\text{chlorobenzene}}{C_6H_5.Cl} + 2Na + \underset{\text{methyl chloride}}{Cl.CH_3} \rightarrow \underset{\text{toluene}}{C_6H_5.CH_3} + 2NaCl$$

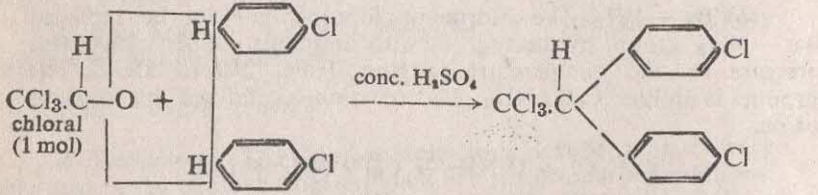
or,



**5. Formation of Gringard reagent.** When chlorobenzene is added to a suspension of magnesium in dry ether, phenylmagnesium chloride is formed.

$$C_6H_5Cl + Mg \xrightarrow{\text{dry ether}} C_6H_5.Mg.Cl$$

**6. Formation of D.D.T.** When chlorobenzene is heated with anhydrous chloral (trichloro-acetaldehyde) in the presence of excess of concentrated sulphuric acid, two molecules of chlorobenzene condense with one molecule of chloral to give dichlorodiphenyltrichloroethane. This substance, usually abbreviated to D.D.T., is a well known insecticide.



chlorobenze (2 mol)

*p*-dichlorodiphenyltrichloroethane (D.D.T.)

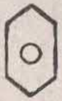
**1 5. Uses.** Chlorobenzene is used in the manufacture of phenol, aniline, D.D.T. (an (insecticide), and *p*-dichlorobenzene (a powerful moth-repellent).

## Questions

1. (*a*) What structural features distinguish aromatic hydrocarbons from aliphatic hydrocarbons ?

(*b*) Explain with one example the term 'aromatic compounds'.

(*c*) Write the general formula of arenes and the formulae and names of the first two arenes.

2. (*a*) What does the graphic formula for benzene  signify :

(*b*) What is the value of the C—C—C angle in benzene ? What does this value suggest ?

3. (*a*) What are main sources of organic compounds ?

(*b*) Write any one reaction by which benzene can be prepared in the laboratory. Give balanced chemical equation for the reaction.

(*c*) Give one *addition* and one substitution reaction for benzene.

(*d*) What is B.H.C. ? What is it used for ? Write its structural formula ?

4. Two compounds A and B have the same empirical formula CH. A is a gaseous aliphatic compound with molecular weight 26; B is a liquid and an aromatic compound with molecular weight 78. Both of them burn with a sooty flame.

(*a*) Give the names of A and B.

(*b*) Write the molecular structures of A and B.

(*c*) Wiil A ordinarily undergo addition reactions or subtitution reactions ?

(*d*) Will B ordinarily undergo addition reactions or substitution reactions ?

(*e*) What will be the products when B is treated with—
*i*. conc. nitric acid in the presence of conc. sulphuric acid,
*ii*. chlorine in the presence of iron, and
*iii*. fuming sulphuric acid ?

5. Show by means of equations the various steps involved in the mechanism of nitration or chlorination of the benzene nucleus.

6. Explain with suitable examples three main differences between the aliphatic and the aromatic compounds.

7. (*a*) What happens when—

*i*. sodium benzoate is heated with soda-lime,

*ii*. benzene is heated with methyl chloride in the presence of anhydrous $AlCl_3$ as catalyst,

*iii*. vapours of phenol are passed over heated zinc.

*iv*. benzene is heated with a mixture of concentrated nitric acid concentrated sulphuric acids ?

8. Write the structural formulae of (*a*) toluene, and (*b*) DDT.

9. Write a short note on either 'the mono-derivatives, di-derivatives, and tri-derivatives of benzene' or 'the orienting effect of groups in the benzene nucleus'.

10. (*a*) Describe in brief two methods for the preparation of chlorobenzene.

(*b*) How are the following subtances made from chlorobenzene ?

*i*. Dichlorobenze
*ii*. Aniline
*iii*. Toluene
*iv*. Phenol
*v*. Benzene
*vi*. DDT.

## Key

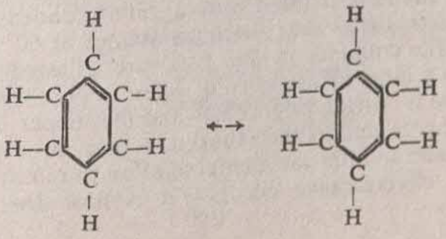
1. See introduction to chapter 28.

2. (*a*) This graphic formula signifies electron delocalization in benzene, *i.e.*, the participitation of $\pi$ electrons in the formation of two bonds.

(*b*) 120° ; it suggests $sp^2$ hybridization of carbon atoms.

4. (*a*) A is acetylene; B is benzene.

(*b*) A : H—C≡C—H;
B :



(*c*) Addition reactions.
(*d*) Substitution reactions.
(*e*) *i*. nitrobenzene, *ii*. chlorobenzene, *iii*. benzenesulphuric acid.

# 29

# Aromatic Nitrogen Compounds

Among the various types of aromatic compounds containing nitrogen, we shall consider in this chapter the representative compounds of two simplest classes of aromatic nitrogen compounds which are of great importance in aromatic chemistry. These are the *nitro-compounds* which contain the $-NO_2$ group attached to benzene nucleus, and the *aryl amines* which have the primary amino group, $-NH_2$, linked directly to a carbon atom of the benzene ring.

The aromatic nitro compounds are not only widely used as explosives but are also the main sources of aromatic amines which are the basic materials for the preparation of azo dyes.

### NITROBENZENE, $C_6H_5NO_2$

## 1. Preparation of Nitrobenzene

**1-1. Laboratory preparation.** Nitrobenzene is prepared in laboratory by nitrating benzene with a mixture of concentrated nitric acid and concentrated sulphuric acid.

$$\underset{\text{benzene}}{C_6H_6} + HNO_3 \xrightarrow{H_2SO_4} \underset{\text{nitrobenzene}}{C_6H_5.NO_2} + H_2O$$

Benzene is added a little at a time to a cooled mixture of the two concentrated acids in a round-bottom flask, with thorough shaking after each addition. Heat is evolved and the flask has to be cooled in a water-bath to keep the temperature below 50°C, or dinitrobenzene will also be formed. When all the benzene has been added the flask is fitted with a reflux condenser and heated for about an hour in a water-bath maintained at 60°C to complete the reaction. The contents of the flask are allowed to cool and then poured into a large excess of cold water. The lower oily layer of nitrobenzene is stirred vigorously and the upper aqueous layer decanted. The product is then shaken in turn in a separating funnel with water and sodium carbonate solution to remove any acids, until no further effervescence occurs. It is now dried with anhydrous calcium chloride and filtered. Crude nitrobenzene containing traces of water is mixed with a little anhydrous zinc chloride and distilled in a flask fitted with an air condenser (Fig. 29-1). The fraction distilling over between 207° and 211° is collected, this being almost pure nitrobenzene.

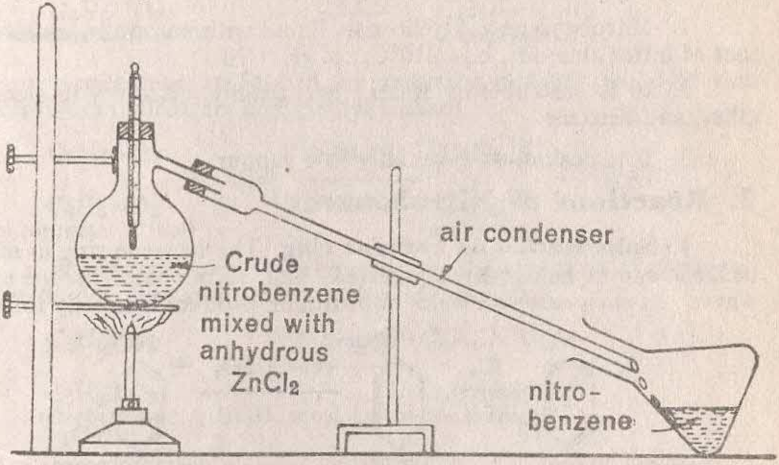


Fig. 29-1 Distillation of crude nitrobenzene.

1-2. **Manufacture**. On a commercial scale also nitrobenzene is prepared by the nitration of benzene. The nitration is carried out in big cast-iron vessels, called nitrators, fitted with stirrers (Fig. 29-2). The mixture of concentrated nitric acid and concentrated sulphuric acid is placed in the vessel and a calculated quantity of benzene slowly run in. The reaction mixture is cooled either by internal cooling coils or by running water between the double walls of the

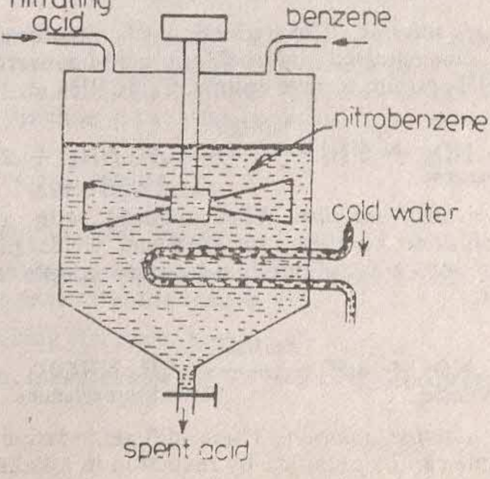


Fig. 29-2. Nitrator (cross-section).

nitrator. At the end, the spent acids are run out and the nitrobenzene layer withdrawn. The nitrobenzene is washed free of acids and then exposed to a current of steam until free from benzene.

## 2. Physical Properties of Nitrobenzene

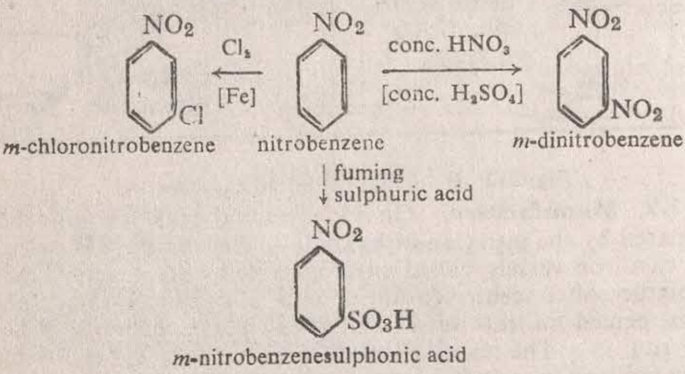
1. Nitrobenzene is a yellowish liquid with an odour resembling that of bitter almonds, b.p. 210°C; sp. gr. 1·20.

2. It is insoluble in water, but readily dissolves in alcohol, ether, and benzene.

3. It is posionous, especially as a vapour.

## 3. Reactions of Nitrobenzene

1. **Substitution on benzene ring**. The benzene ring in nitrobenzene can be halogenated, nitrated, and sulphonated in the usual ways. In each case tho *meta* substitution product is mainly formed.



2. **Reduction**. Nitrobenzene gives a variety of products upon reduction depending upon the reducing agent employed.

(*i*) *In acid solution.* The reduction of nitrobenzene with iron (or tin) and concentrated hydrochloric acid converts the $—NO_2$ group to $—NH_2$ group, to give aniline, $C_6H_5.NH_2$.

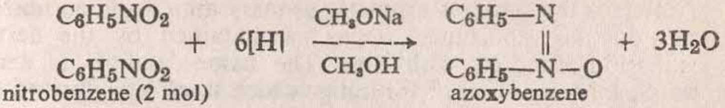
$$\underset{\text{nitrobenzene}}{C_6H_5.NO_2} + 6[H] \xrightarrow{\text{Fe/HCl}} \underset{\text{aniline}}{C_6H_5.NH_2} + 2H_2O$$

(*ii*) *In neutral solution.* When reduced with zinc dust and ammonium chloride solution, nitrobenzene yields phenylhydroxylamine. Reduction with aluminium-mercury couple also gives the same product.

$$\underset{\text{nitrobenzene}}{C_6H_5.NO_2} + 4[H] \xrightarrow{\text{Zn/H}_2\text{O}} \underset{\text{phenylhydroxylamine}}{C_6H_5.NHOH} + H_2O$$

(*iii*) *In alkaline solution.* Three different reduction products of nitrobenzene can be obtained by reduction in alkaline solution.

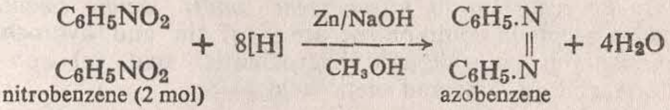
*a. Azoxybenzene* is obtained when nitrobenzene is refluxed with sodium methoxide ($CH_3ONa$) in methyl alcohol solution.



$$\begin{array}{c} C_6H_5NO_2 \\ C_6H_5NO_2 \end{array} + 6[H] \xrightarrow[CH_3OH]{CH_3ONa} \begin{array}{l} C_6H_5{-}N \\ \qquad\ \ \| \\ C_6H_5{-}N{-}O \end{array} + 3H_2O$$

nitrobenzene (2 mol) azoxybenzene

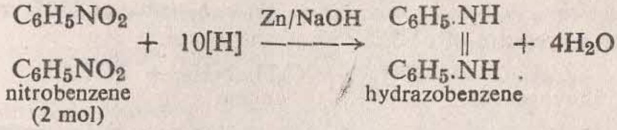
*b. Azobenzene* is formed by reducing nitrobenzene with zinc dust, sodium hydroxide, and methyl alcohol.



$$\begin{array}{c} C_6H_5NO_2 \\ C_6H_5NO_2 \end{array} + 8[H] \xrightarrow[CH_3OH]{Zn/NaOH} \begin{array}{l} C_6H_5.N \\ \qquad\ \| \\ C_6H_5.N \end{array} + 4H_2O$$

nitrobenzene (2 mol) azobenzene

*c. Hydrazobenzene* is produced by the reduction of nitrobenzene with zinc dust and sodium hydroxide solution.



$$\begin{array}{c} C_6H_5NO_2 \\ C_6H_5NO_2 \end{array} + 10[H] \xrightarrow{Zn/NaOH} \begin{array}{l} C_6H_5.NH \\ \qquad\ \| \\ C_6H_5.NH \end{array} + 4H_2O$$

nitrobenzene (2 mol) hydrazobenzene

## 4. Tests for Nitrobenzene

Nitrobenzene is identified by its pale-yellow colour and bitter-almond odour. The presence of the nitro group in the molecule can be established by the following tests :

1. The compound is boiled with zinc dust and ammonium chloride solution, and filtered. The filtrate is warmed with Fehling solution. The formation of a red precipitate of cuprous oxide shows the presence of the nitro group. In these reactions, the nitrobenzene is reduced to phenylhydroxylamine which reduces the Fehling solution.

2. The compound is treated with tin and concentrated hydrochloric acid. The reaction mixture is cooled in an ice-bath and a little sodium nitrite solution is added followed by the addition of a few drops of alkaline β-naphthol solution. An orange-red dye is formed.

## 5. Uses of Nitrobenzene

1. For scenting cheap soaps.

2. For making shoe-polishes; nitrobenzene is an ideal solvent for the dye as it penetrates the leather well.

3. For making floor polishes.

4. For the manufacture of aniline and hydrazobenzene, both by reduction.

5. As a high-boiling solvent and as an oxidizing agent in organic syntheses.

## ANILINE, $C_6H_5.NH_2$

Aniline is the simplest aromatic primary amine and a substance of great industrial importance. It was first obtained by the destructive distillation of indigo with lime. The name 'aniline' is derived from the Spanish word *anil** for indigo **which itself was derived from the Sanskrit word'Neel'.**

## 6. Preparation of Aniline

1. *By the reduction of nitrobenzene under acidic conditions.* Tha reducing agents in common use are : (*a*) tin and hydrochloric acid, (*b*) stannous chloride and hydrochloric acid, (*c*) iron and hydrochloric acid, (*d*) zinc and acetic acid.

$$\underset{\text{nitrobenzene}}{C_6H_5.NO_2} + 6[H] \rightarrow \underset{\text{aniline}}{C_6H_5.NH_2} + 2H_2O$$

2. *By the action of ammonia on chlorobenzene* at 250° to 350°C and under a pressure of about 350 atmospheres.

$$\underset{\text{chlorobenzene}}{C_6H_5Cl} + 2NH_3 \rightarrow \underset{\text{aniline}}{C_6H_5.NH_2} + NH_4Cl$$

3. *By the action of ammonia on phenol* at about 300° in the presence of anhydrous zinc chloride.

$$\underset{\text{phenol}}{C_6H_5OH} + NH_3 \xrightarrow[300^\circ]{ZnCl_2} \underset{\text{aniline}}{C_6H_5.NH_2} + H_2O$$

4. *By the action of bromine and caustic potash on benzamide* (Hoffmann reaction).

$$\underset{\text{benzamide}}{C_6H_5.CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{aniline}}{C_6H_5.NH_2}$$

**6-1. Laboratory preparation.** Aniline is prepared in the laboratory by the reduction of nitrobenzene, using tin and concentrated hydrochloric acid as the reducing agent. The tin reats with hydrochloric acid to give stannous chloride, itself a powerful reducing agent.

$$Sn + 2HCl \rightarrow SnCl_2 + 2[H]$$
$$SnCl_2 + 2HCl \rightarrow SnCl_4 + 2[H]$$
$$C_6H_5.NO_2 + 6[H] \rightarrow C_6H_5.NH_2 + 2H_2O$$

Nitrobenzene and tin are placed in a round-bottom flask fitted with a reflux condenser. The required quantity of concentrated hydrochloric acid is added a little at a time via the condenser, and the mixture gently shaken after each addition. The flask is intermittently cooled by immersion in cold water. When all the acid has been added the condenser is removed and the open flask heated in a boiling water-bath for about half an hour to complete the reduction.

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*Indigo was grown only in India and the Spanish word itself was derived from the Sanskrit *neel* for this material.

The aniline is now present as its chlorostannate, $(C_6H_5.NH_3)_2SnCl_6$. It is liberated by adding an excess of sodium hydroxide solution to the cooled mixture,* and recovered by steam distillation (Fig. 29-3).

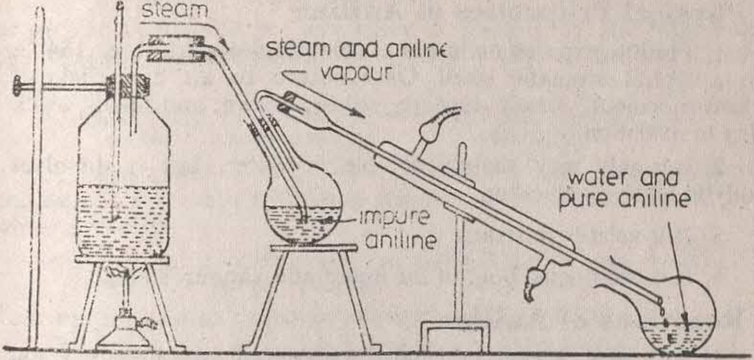

Fig. 29-3. Steam distillation of aniline.

The distillate consisting of a milky emulsion of aniline and water is shaken several times with ether in a separating funnel, and the upper ethereal layer transferred each time into a conical flask. The ethereal solution of aniline is dried with pellets of caustic potash (aniline reacts both with calcium chloride and acidic drying agents). The clear liquid is distilled on a water-bath to drive off ether. The residual aniline is distilled by direct heating over a wire gauge using an air condenser. The fraction boiling over 180—185° is collected; it is pure aniline.

**6-2. Manufacture.** Two methods are in use.

1. *By the reduction of nitrobenzene.* (*a*) Nitrobenzene is reduced with concentrated hydrochloric acid and iron filings (instead of the more expensive tin used in the laboratory preparation). When the reduction is complete, slaked lime is added in excess, and the contents steam distilled. The aniline is recovered from the distillate by distillation under reduced pressure, ether extraction of aniline being uneconomical.

(*b*) Nitrobenzene is dissolved in ethyl alcohol and a catalyst of platinum or nickel suspended in the solution. Hydrogen is passed into the suspension at two or three atmospheres pressure, when nitrobenzene is almost quantitatively reduced to aniline. The catalyst is recovered by filtration, and the aniline is separated from the alcohol by fractional distillation.

$$\underset{\text{nitrobenzene}}{C_6H_5.NO_2} + 3H_2 \xrightarrow{\text{Pt or Ni}} \underset{\text{aniline}}{C_6H_5.NH_2} + 2H_2O$$

2. *By the ammonolysis of chlorobenzene.* Chlorobenzene is heated with a large excess of aqueous ammonia to 200°-350° under a pressure of about 350 atmospheres, in the presence of cuprous

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$^*(C_6H_5.NH_3)_2SnCl_6 + 2NaOH \rightarrow 2C_6H_5.NH_2 + Na_2SnCl_6 + 2H_2O$

chloride. The chlorine atom in chlorobenzene is replaced by the amino group, yielding aniline.

$$C_6H_5.Cl + 2NH_3 \xrightarrow{300^\circ,\ 350\ \text{atm P}} C_6H_5.NH_2 + NH_4Cl$$

## 7. Physical Properties of Aniline

1. Freshly prepared aniline is a colourless liquid, b.p. 184°C, with a typical aromatic smell. On exposure to air and light it darkens in colour, slowly turning yellow, brown, and finally black owing to oxidation.

2. It is only very slightly soluble in water, but it dissolves readily in alcohol and ether.

3. It is volatile in steam.

4. It is poisonous, both in the liquid and vapour states.

## 8. Reactions of Aniline

1. *As a base.* Aniline has basic properties owing to the unshared pair of electrons on the nitrogen atom of the amino group. It accepts a proton from water with the formation of a slight concentration of hydroxyl ion.

$$\underset{\text{aniline}}{C_6H_5.NH_2} + \underset{\text{water}}{HOH} \rightleftharpoons \underset{\text{anilinium hydroxide}}{[C_6H_5.NH_3]OH} \rightleftharpoons \underset{\text{anilinium ion}}{[C_6H_5.NH_3]^+} + \underset{\text{hydroxide ion}}{OH^-}$$

However, aniline is a much weaker base than the aliphatic amines owing to the influence of the electron-attracting phenyl group. Its aqueous solution does not turn litmus blue, although it readily forms soluble, crystalline salts with acids. Since aniline is only weakly basic, its salts are all appreciably hydrolysed in solution giving a strong acid reaction. For the same reason the salt aniline carbonate is not formed. The most important salt of aniline is the hydrochloride which separates as a white solid when aniline is treated with concentrated hydrochloric acid.

$$\underset{\text{aniline}}{C_6H_5.NH_2} + HCl \rightarrow \underset{\substack{\text{anilinium chloride} \\ \text{(phenylammonium chloride)}}}{[C_6H_5.NH_3]Cl}$$

This salt is usually called aniline hydrochloride and is represented by the formula $C_6H_5.NH_2.HCl$. Two other salts of aniline are :

*i.* $[C_6H_5.NH_3]_2SO_4$, anilinium sulphate or phenylammonium sulphate.

*ii.* $[C_6H_5.NH_3]NO_3$, anilinium nitrate or phenylammonium nitrate.

These salts are all decomposed to aniline by adding excess of sodium hydroxide solution in the cold. For example,

$$[C_6H_5.NH_3]Cl + NaOH \rightarrow C_6H_5.NH_2 + NaCl + H_2O$$

Aniline also forms sparingly soluble double salts with chloroplatinic acid, $H_2PtCl_6$, and with the hydrochloric acid solutions of gold chloride and copper chloride (these solutions contain $HAuCl_4$ and $H_2CuCl_4$ respectively). The formulae of these salts are :

$$[C_6H_5.NH_3]_2PtCl_6, [C_6H_5.NH_3]AuCl_4, \text{ and } [C_6H_5.NH_3.]_2CuCl_4$$

2. *Acetylation.* When aniline is treated with acetyl chloride or with acetic anhydride, acetanilide is formed by the replacement of one of the hydrogen atoms of $—NH_2$ group by an acetyl group ($—COCH_3$).

$$\underset{\text{aniline}}{C_6H_5.NH_2} + \underset{\text{acetyl chloride}}{Cl.COCH_3} \rightarrow \underset{\text{acetanilide}}{C_6H_5.NH.COCH_3} + HCl$$

3. *Benzoylation.* When aniline is shaken with benzoyl chloride and excess of sodium hydroxide solution, benzanilide is formed as a white precipitate.

$$\underset{\text{aniline}}{C_6H_5.NH_2} + \underset{\text{benzoyl chloride}}{ClCOC_6H_5} \rightarrow \underset{\text{benzanilide}}{C_6H_5.NH.COC_6H_5} + HCl$$

This reaction is also called Schotten-Baumann reaction.

4. *Alkylation.* Aniline reacts with alkyl halides to yield alkylanilines and quaternary ammonium salts. The reactions occur when aniline is heated with an alkyl halide in a sealed tube. With methyl iodide, for example, the following products are formed :

$$\underset{\text{aniline}}{C_6H_5.NH_2} \xrightarrow[-HI]{CH_3I} \underset{\text{methylaniline}}{C_6H_5.NHCH_3} \xrightarrow[-HI]{CH_3I} \underset{\text{dimethylaniline}}{C_6H_5.N(CH_3)_2}$$

$$\downarrow CH_3I$$

$$\underset{\text{quaternary salt}}{[C_6H_5.N(CH_3)_3]^+I^-}$$

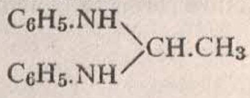
5. *Carbylamine reaction.* Aniline gives the usual carbylamine reaction for aliphatic primary amines when warmed with chloroform and alcoholic potassium hydroxide, forming evil-smelling phenyl isocyanide.

$$\underset{\text{aniline}}{C_6H_5.NH_2} + \underset{\text{chloroform}}{CHCl_3} + 3KOH \rightarrow \underset{\text{phenyl isocyanide}}{C_6H_5.NC} + 3KCl + 3H_2O$$

6. *Condensation with aldehydes.* Aniline condenses with benzaldehyde and also with aliphatic aldehydes when heated on a water bath.

$$\underset{\text{aniline}}{C_6H_5.N}\boxed{H_2 + O}\underset{\text{benzaldehyde}}{HC.C_6H_5} \longrightarrow \underset{\text{benzylidene aniline}}{C_6H_5.N{=}CH.C_6H_5} + H_2O$$

With aliphatic aldehydes, compounds such as



are formed.

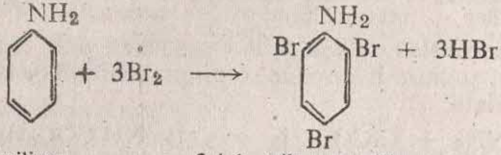
7. *Diazotization.* When aniline dissolved in excess of dilute hydrochloric acid is treated with sodium nitrite solution at 0—5°C, it reacts with the nitrous acid formed to give benzenediazonium chloride in solution

$$\underset{\text{aniline}}{C_6H_5.NH_2} + HNO_2 + HCl \longrightarrow \underset{\text{benzenediazonium chloride}}{C_6H_5.N{\equiv}NCl} + 2H_2O$$

When the solution is heated the diazonium compound decomposes to give phenol.

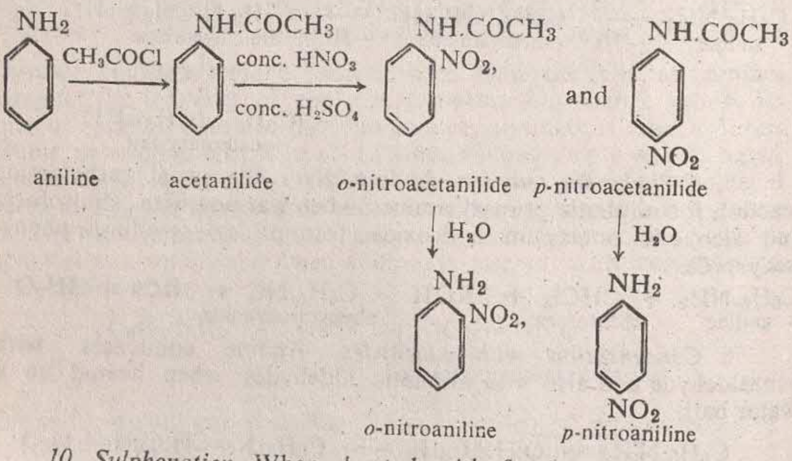
$$C_6H_5.N_2Cl + HOH \longrightarrow \underset{\text{phenol}}{C_6H_5OH} + HCl + N_2\uparrow$$

8. *Halogenation*. The amino group attached to the benzene ring facilitates further substitution on it. Thus when aniline is treated with chlorine water or bromine water, a white precipitate of trichloro- or tribromo-aniline is immediately formed. For example



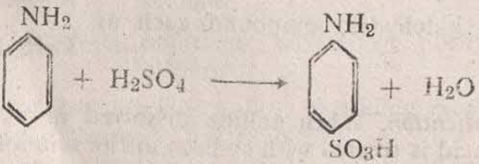
aniline 2,4,6—tribromoaniline

9. *Nitration*. Aniline cannot be nitrated as such since it is rapidly oxidized and charred by concentrated nitric acid. It is therefore first acetylated (to protect the reactive amino group) and then nitrated in the usual manner. The product yields *ortho-* and *para-* nitroanilines when hydrolysed with hot 70 per cent sulphuric acid.



*o*-nitroaniline *p*-nitroaniline

*10. Sulphonation*. When heated with fuming sulphuric acid, aniline forms sulphanilic acid by *para*-substitution.



aniline sulphanilic acid

Sulphanilic acid is used in preparation of dyes and sulphanilamide drugs.

*11. Oxidation.* Aniline is easily oxidized (it darkens by atmospheric oxidation), but the product depends on the oxidizing agent used.

(*i*) Bleaching powder, or sodium hypochlorite solution, oxidizes aniline to a violet-coloured substance (*Runge's test for aniline*).

(*ii*) Acidified potassium dichromate oxidizes aniline to benzoquinone, $C_6H_4O_2$.

(*iii*) Further oxidation produces a black dye, called *aniline black*.

## 9. Tests for Aniline

1. It gives carbylamine reaction.

2. When treated with a few drops of a suspension of bleaching powder, aniline gives a purple colour which soon fades on standing.

3. On adding potassium dichromate to a solution of aniline in sulphuric acid, a dark colour is produced.

4. When aniline is shaken with excess of bromine water, a light pink precipitate of tribromoaniline is formed.

5. When an ice-cold solution of aniline in hydrochloric acid is treated with sodium nitrite and then a few drops of alkaline solution of β-naphthol added to the mixture, a brilliant red colour is obtained.

## 10. Uses of Aniline

1. In the manufacture of antioxidants and vulcanization acceleraters for rubber industry.

2. For making dyes, particularly *azo dyes.*

3. For making acetanilide, sulphanilic acid, nitroanilines, and sulpha drugs.

## 11. Comparison of Aniline and Aliphatic Primary Amines.

**A. Similarities.** Following reactions are given by both aniline and aliphatic primary amines, such as ethylamine.

1. *Formation of salts* with acids, *e.g.*, $C_6H_5.NH_3Cl$ and $C_2H_5.NH_3Cl$.

2. *Isocyanide reaction.* With chloroform and caustic potash, aniline gives phenyl isocyanide, $C_6H_5.NC$; ethylamine gives ethyl isocyanide, $C_2H_5$ NC.

3. *Acetylation.* aniline gives acetanilide. $C_6H_5.NH.COCH_3$; ethylamine gives ethyl acetamide, $C_2H_5.NH.COCH_3$.

4. *Benzoylation.* Aniline gives benzanilide, $C_6H_5.NH.CO.C_6H_5$; ethylamine gives $C_2H_5.NH.CO.C_6H_5$.

5. *Reactions with alkyl halides.* In both cases quaternary salts are the ultimate products; $[C_6H_5N(C_2H_5)_3]^+I^-$ and $[(C_2H_5)_4N]^+I^-$ with ethyl iodide.

**B. Differences.** Aniline differs from aliphatic primary amines in the following respects :

1. *Physical properties.* Aliphatic primary amines are low-boiling substances with the odour of ammonia, and very soluble in water. Aniline is a high-boiling liquid with an aromatic smell, and only slightly soluble in water.

2. *Basic character.* Aliphatic amines have pronounced basic properties; in contrast, aniline is a very weak base.

3. *Reaction with nitrous acid.* When treated with nitrous acid, aliphatic amines give alcohols, *e.g.*,

$$C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + H_2O + N_2$$

aniline gives diazonium salts such as benzenediazonium chloride, $C_6H_5N_2Cl$.

4. *Reactions of benzene ring.* Aniline undergoes halogenation, nitration, and sulphonation; these reactions are not given by aliphatic amines.

5. *Oxidation.* Aniline is readily oxidized giving various coloured products with various oxidizing agents; aliphatic amines are not easily oxidized.

## Questions

1. (*a*) How can you prepare a dry sample of nitrobenzene in the laboratory ?

(*b*) Mention two physical properites of nitrobenzene.

(*c*) Give two reactions of nitrobenzene in which substitution occurs on the benzene ring.

2. Indicate a method by which each of the following conversions may be effected. Give balanced equation for the reactions.

*i.* Benzene to nitrobenzene.

*ii.* Nitrobenzene to aniline.

*iii.* Aniline to acetanilide.

3. (*a*) How is aniline prepared in the laboratory.

(*b*) Discuss the basic nature of aniline. Why does it not form the salt aniline carbonate ?

(*c*) Give the names and formulae of products obtained by the bromination and sulphonation of aniline.

4. Write balanced equations, indicating the names of organic reactants and products, for the following reactions :

1. Nitration of aniline.
2. Carbylamine reaction.
3. Alkylation of aniline.

5. (*a*) How would you distinguish between nitrobenzene and aniline by a chemical test ?

(*b*) Give two important uses each of aniline and nitrobenzene.

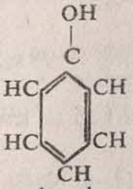
□ □

# 30

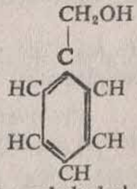
# Phenol, Benzaldehyde, and Benzoic Acid

Phenol, benzaldehyde, and benzoic acid are the representative compounds of the important classes of aromatic compounds, the *phenols*, the aromatic aldehydes, and the aromatic *monocarboxylic acids* respectively.

Phenols are the hydroxy derivatives of aromatic hydrocarbons in which the hydroxyl group is directly linked to carbon atoms of the benzene ring. If the hydroxyl group is linked to the benzene ring by a carbon atom as part of a side chain, the compound is not a phenol but an aromatic alcohol, *e.g.*, benzyl alcohol.



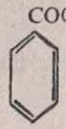
phenol



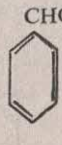
benzyl alcohol

An interesting fact about phenol is that it was the first compound to be employed specifically as an antiseptic (Lister, 1867) under the name carbolic acid. Now it has been largely replaced for this purpose by many more effective and safer phenol derivatives.

Benzoic acid is the simplest of all aromatic carboxylic acids, and consists of a benzene ring with a carboxyl group directly attached to it.



Benzaldehyde is the simplest of all aromatic aldehydes and consists of an aldehyde group directly attached to the benzene ring.



## PHENOL, $C_6H_5OH$

## 1. Preparation of Phenol

**1-1. Laboratory preparation.** Two methods are available :

1. *By the hydrolysis a diazonium salt.* Aniline is dissolved in dilute sulphuric acid and the solution treated with a slight excess of sodium nitrite solution at 0—5°C. The resulting benzendiazonium hydrogen sulphate is hydrolysed to phenol by warming the solution to 50-60°C.

$$\underset{\substack{\text{benzenediazonium}\\ \text{hydrogen sulphate}}}{C_6H_5N_2HSO_4} + HOH \longrightarrow \underset{\text{phenol}}{C_6H_5OH} + H_2SO_4 + N_2\uparrow$$

The phenol is separated from tarry products by steam distillation, and extracted with ether. The ethereal solution is dried with anhydrous potassium carbonate and then distilled using an air condenser.

2. *From sodium benzenesulphonate.* Benzene is sulphonated to benzenesulphonic acid which is converted to its sodium salt. Sodium benzenesulphonate is fused with sodium hydroxide at 250°C in a nickel crucible, when sodium phenate is formed.

$$\underset{\text{sodium benzenesulphonate}}{C_6H_5.SO_3Na} + 2NaOH \xrightarrow{250^\circ} \underset{\text{sodium phenate}}{C_6H_5.ONa} + Na_2SO_3 + H_2O$$

The residue is dissolved in water and acidified to liberate phenol, which separates as an oily layer.

$$\underset{\text{sodium phenate}}{C_6H_5.ONa} + HCl \longrightarrow \underset{\text{phenol}}{C_6H_5OH} + NaCl$$

3. *From Grignard reagents.* Phenol is formed when a phenylmagnesium halide (Grignard reagent) is treated with oxygen and the resulting product hydrolysed with a mineral acid. For example,

$$\underset{\substack{\text{phenylmagnesium}\\ \text{bromide}}}{C_6H_5.MgBr} \xrightarrow{\frac{1}{2}O_2} C_6H_5.OMgBr \xrightarrow{H\ |\ OH} \underset{\text{phenol}}{C_6H_5OH} + Mg\left\langle{}^{OH}_{Br}\right.$$

**1-2. Manufacture.** Phenol is commercially prepared from the following sources :

1. *From coal-tar. The middle-oil* distillation fraction of coal-tar collected between 170-230°C contains phenol ($C_6H_5OH$), isomeric cresols* ($CH_3.C_6H_4.OH$), and naphthalene ($C_{10}H_8$). The naphthalene

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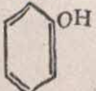
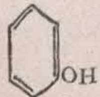
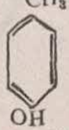
*These are hydroxytoluenes (*o, m, p*), and the next homologues of phenol



o-cresol



m-cresol



p-cresol

is removed from the middle-oil by crystallization and the residue shaken with sodium hydroxide solution, which dissolves the phenols. For example,

$$C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O$$

The aqueous layer is separated and saturated with carbon dioxide to liberate the phenols.

$$2C_6H_5ONa + CO_2 + H_2O \longrightarrow 2C_6H_5OH + Na_2CO_3$$

Phenol is isolated from the resulting mixture by fractional distillation. Crystals of pure phenol are deposited on cooling the distillate.

Formerly all phenol was obtained from coal-tar, but the demand for phenol now far exceeds the supply of it from this source. As such other industrial processes are also in regular use for its preparation.

2. *From chlorobenzene.* Chlorobenzene is hydrolyzed to phenol by heating it with sodium hydroxide solution to 300—350°C under a pressure of 200 atmospheres (*Dow process*).

$$C_6H_5Cl + 2NaOH \xrightarrow{300^\circ\text{C}, \ 200 \text{ atm P}} C_6H_5ONa + NaCl + H_2O$$

The phenol is liberated from its sodium salt by carbon dioxide, and removed from the other reaction products by steam distillation.

3. *From benzene.* A mixture of benzene vapour, hydrogen chloride, and air is passed over a copper catalyst at 230°C, when chlorobenzene is formed.

$$\underset{\text{benzene}}{2C_6H_6} + 2HCl + \underset{\text{(from air)}}{O_2} \xrightarrow{\text{Cu, } 230^\circ} \underset{\text{chlorobenzene}}{2C_6H_5Cl} + 2H_2O$$

The chlorobenzene is hydrolyzed to phenol by mixing it with steam and passing the mixture over a silicon catalyst at 500°C

$$\underset{\text{chlorobenzene}}{C_6H_5Cl} + H_2O \xrightarrow{\text{Si, } 500^\circ} \underset{\text{phenol}}{C_6H_5OH} + \underset{\text{(regenerated)}}{HCl}$$

This German process, called *Raschig process*, is unique in that it consumes only air and benzene in the preparation of phenol. The method, like the Dow process (see above), uses chlorobenzene as an intermediate product, but prepares the compound by the air oxidation of hydrochloric acid which is regenerated in the hydrolysis of chlorobenzene.

4. *From sodium benezenesulphonate.* The commercial method differs from the laboratory preparation of phenol from this compound described above in certain details. In the first step, benzenesulphonic acid is made by heating benzene with concentrated sulphuric acid to about 175°. The high temperature employed is not required for sulphonation but is used to shift the equilibrium to the right by removing the water as it forms.

$$\underset{\text{benzene}}{C_6H_6} + H_2SO_4 \overset{175^\circ}{\rightleftharpoons} \underset{\text{benzenesulphonic acid}}{C_6H_5.SO_3H} + H_2O$$

The sulphonic acid is converted to the sodium salt which is then fused with sodium hydroxide at about 300° to yield sodium phenate $C_6H_5ONa$.

$$\underset{\text{sodium benzenesulphonate}}{C_6H_5.SO_3Na} + 2NaOH \xrightarrow{300^\circ} \underset{\text{sodium phenate}}{C_6H_5ONa} + Na_2SO_3 + H_2O$$

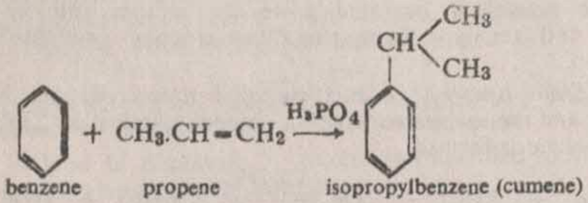
The sodium sulphite, $Na_2SO_3$, obtained in the reaction is used to convert the next batch of benzenesulphonic acid to its sodium salt.

$$2C_6H_5.SO_3H + Na_2SO_3 \rightarrow 2C_6H_5.SO_3Na + H_2O + SO_2$$

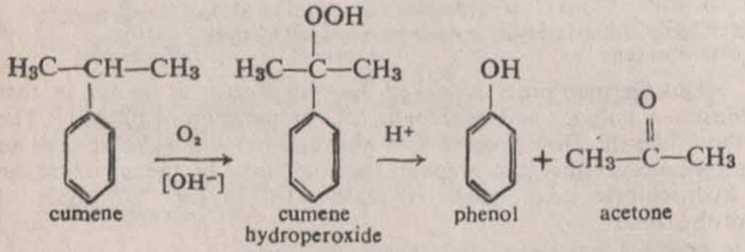
The sulphur dioxide evolved is passed into sodium phenate solution to liberate phenol.

$$\underset{\text{sodium phenate}}{2C_6H_5ONa} + H_2O + SO_2 \rightarrow \underset{\text{phenol}}{2C_6H_5OH} + Na_2SO_3$$

5. *From isopropylbenzene* (*cumene*). Benzene and propylene are combined into isopropylbenzene or cumene by compressing to 30 atmospheres and passing over a catalyst of phosphoric acid at 250°.



The cumene, under slightly basic conditions, is oxidized by air to cumene hydroperoxide, which is decomposed into phenol and acetone by treatment with sulphuric acid.



## 2. Physical Properties of Phenol

1. Phenol is a colourless hygroscopic, crystalline solid, m.p. 42°C, b.p. 181°C, with a characteristic odour. On exposure to light and air it develops a slight pink colour due to partial oxidation.

2. It is only moderately soluble in water at room temperature, but is completely miscible with it above 68°C, the critical solution temperature. It dissolves readily in alcohol, ether, and benzene.

3. It is poisonous and blisters the skin on contact.

## 3. Reactions of Phenol

The chemical reactions of benzene fall into two broad groups: (1) those which involve the hydroxyl group, and (2) those which produce substitution on the benzene ring.

**A. Reactions of the hydroxyl group.** These are:

1. *As an acid.* Phenol is very weakly acidic, dissociating in aqueous solution into the phenoxide and hydrogen ions.

$$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$$

It dissolves in alkalis forming salts called phenates or phenoxides. For example,

$$\underset{\text{phenol}}{C_6H_5OH} + NaOH \rightarrow \underset{\substack{\text{sodium phenate}\\ \text{(sodium phenoxide)}}}{C_6H_5ONa} + H_2O$$

However, it is weaker than even carbonic acid* and does not affect litmus. Phenol can be liberated from its salts by the introduction of carbon dioxide in solution, a reaction often used to separate phenol from a more strongly acidic compound such as benzoic acid.

$$2C_6H_5ONa + H_2O + CO_2 \rightarrow 2C_6H_5OH + Na_2CO_3$$

2. *Reaction with sodium.* In dry ethereal solution phenol reacts with sodium, liberating hydrogen and forming sodium phenate.

$$2C_6H_5OH + 2Na \rightarrow 2C_6H_5ONa + H_2\uparrow$$

3. *Reduction to benzene.* Phenol is reduced to benezene when its vapour is passed over red-hot zinc dust.

$$\underset{\text{phenol}}{C_6H_5OH} + Zn \rightarrow \underset{\text{benzene}}{C_6H_6} + ZnO$$

4. *Ether formation.* The sodium salt of phenol, sodium phenate, reacts with alkyl halides (such as ethyl iodide) to give ethers.

$$\underset{\text{sodium phenate}}{C_6H_5ONa} + \underset{\text{ethyl iodide}}{IC_2H_5} \rightarrow \underset{\text{phenyl ethyl ether}}{C_6H_5.O.C_2H_5} + NaI$$

5. *Acetylation (ester formation).* Phenol readily reacts with acetyl chloride or acetic anhydride to give the ester, phenyl acetate.

$$\underset{\text{phenol}}{C_6H_5OH} + \underset{\text{acetyl chloride}}{ClCOCH_3} \rightarrow \underset{\text{phenyl acetate}}{C_6H_5.COO.CH_3} + HCl$$

6. *Benzoylation.* If phenol is shaken with benzoyl chloride and excess of sodium hydroxide solution, it is benzoylated to give the ester, phenyl benzoate (*Schotten-Baumann reaction*).

$$\underset{\text{phenol}}{C_6H_5OH} + \underset{\text{benzoyl chloride}}{Cl.COC_6H_5} \rightarrow \underset{\text{phenyl benzoate}}{C_6H_5.COO.C_6H_5} + HCl$$

7. *Reaction with phosphorus pentachloride.* Phenol reacts with phosphorus pentachloride at room temperature to give phenyl chloride (chlorobenzene) and hydrogen chloride.

$$\underset{\text{phenol}}{C_6H_5OH} + PCl_5 \rightarrow \underset{\text{phenyl chloride}}{C_6H_5Cl} + POCl_3 + HCl\uparrow$$

---

*The ionization constant of phenol (K) is $1{\cdot}3\times10^{-10}$, that of carbonic acid is $4{\cdot}3\times10^{-7}$.

The yield of phenyl chloride is poor, the main product being triphenyl phosphate.

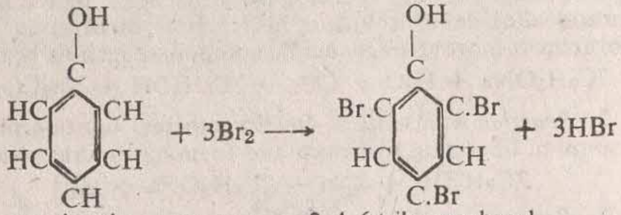
$$\underset{\text{phenol}}{3C_6H_5OH} + POCl_3 \longrightarrow \underset{\text{triphenyl phosphate}}{(C_6H_5)_3PO_4} + 3HCl$$

8. *Reaction with ammonia.* When phenol is heated with ammonia to 300°C in an autoclave in the presence of zinc chloride as the catalyst, it is converted into aniline.

$$\underset{\text{phenol}}{C_6H_5OH} + NH_3 \xrightarrow{300°,\ ZnCl_2} \underset{\text{aniline}}{C_6H_5.NH_2} + H_2O$$

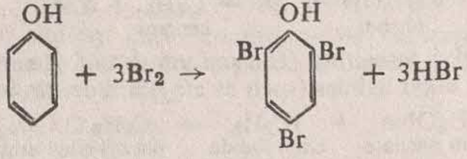
8. **Reactions of ring substitution**. The main reactions of this class are :

1. **Halogenation**. When an aqueous solution of phenol is treated with chlorine water or bromine water, a white precipitate of 2, 4, 6—trichloro- or tribromophenol is immediately formed.

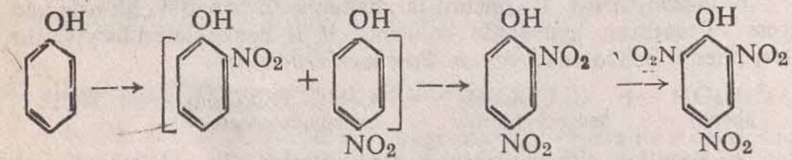


phenol 2, 4, 6-tribromophenol

Or, more simply,



2. **Nitration**. When phenol is treated with moderately concentrated nitric acid, a mixture of ortho- and para-nitrophenols, is formed. Concentrated nitric acid forms 2, 4-dinitrophenol, and concentrated nitric acid in the presence of concentrated sulphuric acid gives 2, 4, 6-trinitrophenol, commonly known as picric acid.*



phenol *o*-nitrophenol *p*-nitrophenol 2, 4-dinitrophenol 2, 4, 6-trinitrophenol

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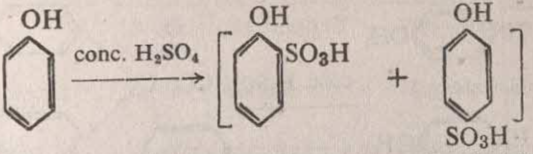
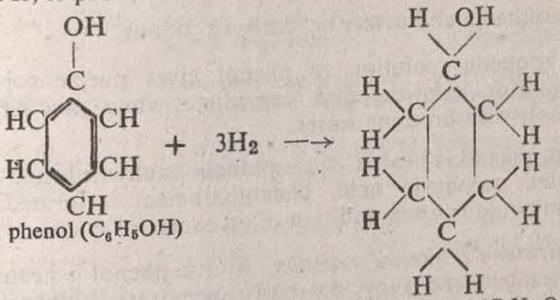
*The nitro groups on the benzene ring increase the dissociation of the OH groups, so that nitrophenols are more strongly acidic than phenol. Unlike phenol, they liberate carbon dioxide from sodium carbonate solution. They are all bright yellow in colour. Trinitrophenol, m.p. 122°C, is a fairly strong acid, usually called picric acid. It is used as a high explosive, as a dye to colour wool or silk yellow, and as an antiseptic in the treatment of burns.

3. *Sulphonation.* When treated with concentrated sulphuric acid phenol gives a mixture of ortho- and para-phenolsulphonic acids.



phenol o-phenolsluphonic acid p-phenolsulphonic acid

4. *Hydrogenation.* When hydrogen is passed through phenol at 150°C in the presence of a finely divided nickel catalyst, cyclohexanol, $C_6H_{11}OH$, is produced.

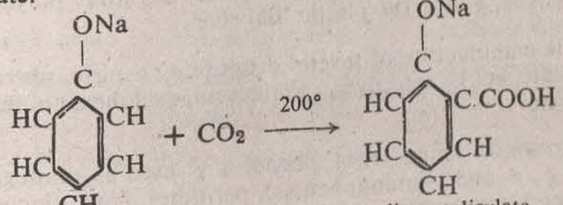


phenol ($C_6H_5OH$)

cyclohexanol ($C_6H_{11}OH$)

Cyclohexanol is a secondary alcohol (functional group, >CHOH) and does not belong to the class of phenols.

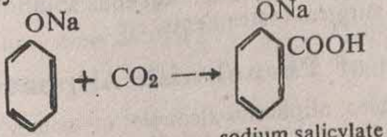
5. *Kolbe's reaction.* When the sodium salt of phenol, sodium phenate, is heated to about 200°C in a stream of carbon dioxide, a carboxyl group is introduced in the benzene ring giving sodium salicylate.



sodium phenate

sodium salicylate

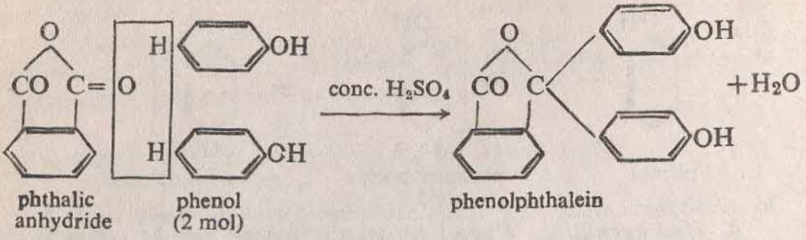
Or, more simply



sodium phenate sodium salicylate

6. *Condensation with phthalic anhydride.* When heated with phthalic anhydride and a suitable dehydrating agent (*e.g.* concentrated

sulphuric acid), phenol will undergo a condensation reaction to form phenolphthalein.



## 4. Tests for Phenol

1. Phenol has a characteristic 'carbolic' odour.

2. An adqueous solution of phenol gives purple coloration with ferric chloride solution, and immediate white precipitate (of tribromophenol) with bromine water.

3. When phenol is heated with phthalic anhydride and a drop of concentrated sulphuric acid, phenolphthalein is formed. This produces a pink colour upon addition of an excess of alkali solution.

4. *Liebermann's 'nitroso' reaction*. A little phenol is heated with a little sodium nitrite and a few drops of concentrated sulphuric acid. A bluish green or intense blue colour develops. When the product is poured into water the colour changes to red, turning blue again when excess of alkali is added.

## 5. Uses of Phenol

1. In the manufacture of phenolic resins and plastics. Under carefully controlled conditions phenol condenses and polymerizes with formaldehyde, giving the plastic 'Bakelite'.

2. In the manufacture of several drugs (*e.g.*, aspirin, phenacitin, sodium salicylate, etc.), azo dyes, picric acid, cyclohexanol (used to make nylon), etc.

3. Compounds made from phenol are used as photographic developers (*e g.*, *o*- and *p*-aminophenols), perfumes, flavouring agents, detergents, wood preservatives, and selective weedkillers.

4. As a disinfectant in dilute aqueous solutions to disinfect premises, furniture, surgical instruments, etc.

## 6. Comparison of Phenol with Aliphatic Alcohols

Phenol resembles aliphatic alcohols in some properties but differs from them in others. In Table 30-1, the properties and reactions of phenol are compared with those of a typical aliphatic primary alcohol, ethyl alcohol.

Table 26-1 *Comparison of phenol and ethyl alcohol*

| Property/Reaction | Phenol, $C_6H_5OH$ | Ethyl alcohol, $C_2H_5OH$ |
|---|---|---|
| 1. Odour | Characteristic 'carbolic' odour. | Wine-like odour. |
| 2. Miscibility with water (20°C). | Partially miscible. | Miscible in all proportions. |
| 3. With alkalis | Weakly acidic, forms salts. | Neutral, does not form salts. |
| 4. Action of sodium | Forms sodium derivative, $C_6H_5ONa$ and hydrogen. | Forms sodium derivative, $C_2H_5ONa$ and hydrogen. |
| 5. Reduction to hydrocarbon | Reduced to benzene, $C_6H_6$, when heated with zinc. | Reduced to ethane, $C_2H_6$ when refluxed with HI. |
| 6. With alkyl halides | Sodium salt reacts to give phenyl ethyl ether | Sodium derivative reacts to give diethyl ether. |
| 7. Action of $CH_3COCl$ | Acetylates readily to give the ester, phenyl acetate. | Acetylates readily to give the ester ethyl acetate. |
| 8. Action of $C_6H_5COCl$ and NaOH | Benzoylates readily to give phenyl benzonate. | Benzoylates readily to give ethyl benzoate. |
| 9. Action of $PCl_5$ | Slow reaction, poor yield of $C_6H_5Cl$. | Vigorous reaction, high yield of $C_2H_5Cl$. |
| 10. Hydrogenation | Adds hydrogen to give cyclohexanol. | Does not add hydrogen. |
| 11. Action of chlorine water or bromine water. | Immediately give a white precipitate of tricbloro or tribromophenol. | None. |
| 12. Action of nitric acid. | Nitration occurs. | None |
| 13. Action of sulphuric acid. | Sulphonation occurs. | None. |
| 14. Kobe's reaction | Gives salicylic acid. | Does not occur. |
| 15. With phthalic anhydride | Condenses in presences of conc. $H_2SO_4$ to give phenolpthaline. | No reaction. |
| 16. Action of organic acids | None. | Forms ethyl esters. |
| 17. Action of halogen hydracids, HCl, HBr, HI. | None. | Forms alkyl halides. |
| 18. Iodoform reaction | Does not occur. | Occurs readily. |
| 19. Action of aq. $FeCl_3$ | Purple coloration. | None |
| 20. Action of alkaline $KMnO_4$. | Gives several products. | None |
| 21. Dehydrogenation | Does not occur. | Gives acctaldehyde. |

## BENZALDEHYDE, $C_6H_5.CHO$

## 7. Preparation of Benzaldehyde

**7-1. Laboratory preparation** (1) Benzaldehyde is usually made in the laboratory by boiling benzyl chloride with a solution of cupric nitrate or lead nitrate under reflux for several hours. First, benzyl chloride is hydrolyzed to give benzyl alcohol and then benzyl alcohol is oxidized to benzaldehyde.

$$\underset{\text{benzyl chloride}}{C_6H_5.CH_2Cl} + H_2O \rightarrow \underset{\text{benzyl alcohol}}{C_6H_5.CH_2OH} + HCl$$

$$\underset{\text{benzyl alcohol}}{C_6H_5.CH_2OH} + [O] \rightarrow \underset{\text{benzaldehyde}}{C_6H_5.CHO} + H_2O$$

A stream of carbon dioxide is passed through the mixture to remove oxides of nitrogen formed by the decomposition of the metal nitrate. The benzaldehyde is extracted with ether, dried over anhydrous calcium chloride, and distilled. It can be further purified by forming a crystalline addition compound with sodium bisulphite and distilling the compound with dilute sulphuric acid.

(2) *By oxidizing toluene* with chromyl chloride, $CrO_2Cl_2$, or with manganese dioxide and moderately concentrated sulphuric acid at 40°C.

$$\underset{\text{toluene}}{C_6H_5.CH_3} + 2[O] \rightarrow \underset{\text{benzaldhyde}}{C_6H_5.CHO} + H_2O$$

The benzaldehyde formed is removed by extraction with a solvent.

**7-2. Manufacture**. Benzaldehyde is manufactured by the oxidation of toluene. In one process, the oxidation is effected by warming benzaldehyde with manganese dioxide and sulphuric acid. In another one, toluene is oxidized directly by passing its vapour, mixed with air and excess of nitrogen, over a catalyst of manganese dioxide or vanadium pentoxide at 500°C.

$$\underset{\text{toluene}}{C_6H_5.CH_3} + O_2 \xrightarrow{V_2O_5;\,500\ C} \underset{\text{benzaldehyde}}{C_6H_5.CHO} + H_2O$$

## 8· Physical Properties of Benzaldehyde

1. Benzaldehyde is a colourless liquid, with a smell of bitter almonds; b.p. 179°C, sp. gr. 1·05.

2. It is only sparingly soluble in water, but dissolves readily in organic solvents.

3. It is volatile in steam.

## 9. Reactions of Benzaldehyde

The reactions of benzaldehyde are those of the —CHO group and the benzene nucleus. In some of the reactions due to —CHO group, benzaldehyde resembles aliphatic aldehydes, while in others it differs from them.

### 9-1. Reactions of —CHO group common with aliphatic aldehydes

1. *Oxidation.* Upon exposure to the air at room temperature benzaldehyde is finally oxidized to benzoic acid. The oxidation occurs rapidly when benzaldehyde is warmed with acidified potassium permanganate solution.

$$\underset{\text{benzaldehyde}}{C_6H_5.CHO} + [O] \rightarrow \underset{\text{benzoic acid}}{C_6H_5.COOH}$$

Due to the ease of its oxidation, benzaldehyde is a strong reducing agent. It reduces Tollen's reagent (ammoniacal silver nitrate) forming a mirror of silver. However, it does not reduce Fehling's solutions.

2. *Reduction.* When treated with sodium amalgam and water benzaldehyde is reduced to benzyl alcohol ($—CHO \rightarrow CH_2OH$).

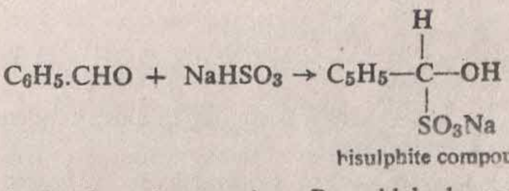
$$\underset{\text{benzaldehyde}}{C_6H_5.CHO} + 2[H] \rightarrow \underset{\text{benzyl alcohol}}{C_6H_5.CH_2OH}$$

A stronger reducing agent such as amalgamated zinc and concentrated hydrochloric acid reduces benzaldehyde to toluene (*Clemmensen reduction*)

$$C_6H_5.CHO + 4[H] \rightarrow C_6H_5.CH_3 + H_2O$$

3. *Addition reactions.* Benzaldehyde forms addition compounds with hydrogen cyanide and sodium bisulphite.

$$\underset{\text{benzaldehyde}}{C_6H_5.CHO} + HCN \rightarrow \underset{\substack{\text{benzaldehyde cyanohydrin}\\ \text{or, mandelonitrile}}}{C_6H_5(OH)CN}$$



$$C_6H_5.CHO + NaHSO_3 \rightarrow C_5H_5—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle SO_3Na}{|}}{C}}—OH$$

bisulphite compound

4. *Condensation reactions.* Benzaldehyde condenses with hydroxylamine, phenylhydrazine, and semicarbazide to give the oxime, phenylhydrazone, and semicarbazone respectively.

$$\underset{\text{benzaldehyde}}{C_6H_5.CHO} + \underset{\text{hydroxylamine}}{H_2N.OH} \rightarrow \underset{\text{benzaldoxime}}{C_6H_5.CH{=}NOH} + H_2O$$

$$\underset{\text{benzaldehyde}}{C_6H_5.CHO} + \underset{\text{phenylhydrazine}}{H_2N.NH.C_6H_5} \rightarrow \underset{\text{benzaldehyde phenylhydrazone}}{C_6H_5.CH{=}N.NH.C_6H_5} + H_2O$$

$$\underset{\text{benzaldehyde}}{C_6H_5.CHO} + \underset{\text{semicarbazide}}{H_2N.NH.CO.NH_2} \rightarrow \underset{\text{benzaldehyde semicabazone}}{C_6H_5.CH{=}N.NH.CONH_2} + H_2O$$

5. *With $PCl_5$.* Benzaldehyde reacts with phosphorus pentachloride to give benzal chloride.

$$\underset{\text{benzaldehyde}}{C_6H_5.CHO} + PCl_5 \rightarrow \underset{\text{benzal chloride}}{C_6H_5.CHCl_2} + POCl_3$$

6. *With Schiff's reagent*. It reduces the pink colour of Schiff's reagent.

**9-2. Reactions of —CHO group not given by aliphatic aldehydes.**

1 *Condensation with ammonia*. Benzaldehyde condenses with ammonia to give hydrobenzamide (aliphatic aldehydes give aldehyde-ammonias).

$$\underset{\text{benzaldehyde}}{3C_6H_5.CHO} + 2NH_3 \rightarrow \underset{\text{hydrobenzamide}}{(C_6H_5.CH)_3N_2} + 3H_2O^*$$

2. *Condensation with primary amines*. Benzaldehyde condenses with primary amines to form Schiff's bases, *e.g*, benzalaniline with benzaldehyde.

$$\underset{\text{benzaldehyde}}{C_6H_5.CHO} + \underset{\text{aniline}}{H_2N.C_6H_5} \rightarrow \underset{\text{benzalaniline}}{C_6H_5.CH{=}N.C_6H_5} + H_2O$$

3. *Cannizaro reaction*. When warmed with a concentrated solution of alkali, *e.g.*, potassium hydroxide, one molecule of benzaldehyde is oxidized to benzoic acid and the other is reduced to benzyl alcohol.

$$\underset{\text{benzaldehyde}}{2C_6H_5.CHO} + KOH \rightarrow \underset{\text{pot. benzoate}}{C_6H_5.COOK} + \underset{\text{benzyl alcohol}}{C_6H_5.CH_2OH}$$

Cannizaro reaction is given by all aromatic aldehydes and among the aliphatic aldehydes only by formaldehyde.

4. *Benzoin condensation*. When heated with alcoholic potassium cyanide, two molecules of benzaldehyde condense to give benzoin, a keto-alcohol.

$$\underset{\text{benzaldehyde}}{C_6H_5.CHO} + \underset{\text{benzaldehyde}}{OHC.C_6H_5} \xrightarrow{\text{alc. KCN}} \underset{\text{benzoin}}{C_6H_5.CH(OH).CO.C_6H_5}$$

Note that benzoin condensation is similar to aldol condensation studied in the case of acetaldehyde.

5. *With acetic anhydride*. When benzaldehyde is heated with acetic anhydride in the presence of sodium acetate, an unsaturated acid— cinnamic acid is formed. This reaction is known as *Perkin's reaction*.

$$\underset{\text{benzaldehyde}}{C_6H_5.CHO} + \underset{\text{acetic anhydride}}{(CH_3.CO)_2O} \xrightarrow{CH_3.COONa} \underset{\text{cinnamic acid}}{C_6H_5.CH{=}CH.COOH} + CH_3.COOH$$

**9-3. Reactions of the benzene nucleus**. Benzaldehyde gives the usual nuclear substitution reactions, the new group entering the meta position with respect to the —CHO group. Thus with chlorine

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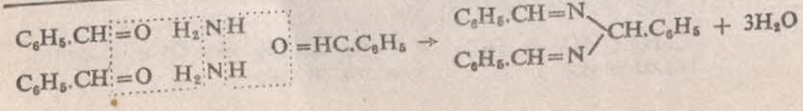
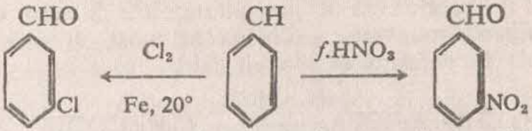


$$\begin{matrix} C_6H_5.CH{=}O \quad H_2N.H \\ C_6H_5.CH{=}O \quad H_2N.H \end{matrix} \quad O{=}HC.C_6H_5 \rightarrow \begin{matrix} C_6H_5.CH{=}N \\ C_6H_5.CH{=}N \end{matrix} \!\!> CH.C_6H_5 + 3H_2O$$

in the presence of iron filings or iodine (catalyst) it gives meta-chlorobenzaldehyde and with fuming nitric acid, *m*-nitrobenzaldehyde.



*m*-chlorobenzaldehyde benzaldehyde *m*-nitrobenzaldehyde

## 10. Tests for Benzaldehyde

1. Benzaldehyde gives a silver mirror when heated with ammoniacal silver nitrate, but has no action on Fehling's solution.

2. It gives a white precipitate when shaken with a concentrated solution of sodium bisulphite, and a yellow precipilate when treated with phenylhydrazine dissolved in acetic acid (acetaldehyde reacts with these reagents, but the products are too soluble to be precipitated).

3. When benzaldehyde is warmed with acidified potassium permanganate solution, it is decolorized and a white precipitate of benzoic acid is formed.

## 11. Uses of Benzaldehyde

1. As a cherry-type flavouring material in perfumery.
2. In the mancfacture of dyes, *e.g.*, malachite green.
3. As a starting material in various types of syntheses.

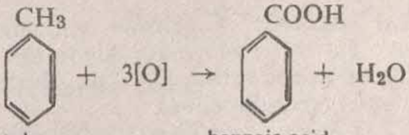
BENZOIC ACID, $C_6H_5.COOH$

## 12. Preparation of Benzoic Acid

1. *By the oxidation of toluene*. When toluene is heated under reflux with acidified potassium dichromate, the side chain (—$CH_3$) is oxidized to carboxyl group forming benzoic acid.

$$\underset{\text{toluene}}{C_6H_5.CH_3} + 3[O] \rightarrow \underset{\text{benzoic acid}}{C_6H_5.COOH} + H_2O$$

or,



toluene benzoic acid

2. *By the hydrolysis of benzotrichloride*. Toluene is first chlorinated to benzotrichloride which yields benzoic acid upon hydrolysis. This method gives better yield than direct oxidation of toluene.

$$\underset{\text{toluene}}{C_6H_5.CH_3} \xrightarrow[-3HCl]{3Cl_2} \underset{\text{benzotrichloride}}{C_6H_5.CCl_3} \xrightarrow{3H_2O} \underset{\text{orthobenzoic acid (unstable)}}{C_6H_5.C(OH)_3} \xrightarrow{-H_2O} \underset{\text{benzoic acid}}{C_6H_5.COOH}$$

3. *By the oxidation of benzaldehyde.* Benzaldehyde is heated with an alkaline solution of potassium permanganate. The resulting benzoic acid remains in solution as sodium benzoate. On acidification, benzoic acid is liberated as a precipitate; it is filtered, washed well, and recrystallized from water. This is the most suitable method for the laboratory preparation of benzoic acid.

$$\underset{\text{Benzaldehyde}}{C_6H_5.CHO} + [O] \xrightarrow{\text{alk.}KMnO_4} \underset{\text{benzoic acid}}{C_6H_5.COOH}$$

Benzyl alcohol, $C_6H_5CH_2.OH$, can be similarly oxidized to benzoic acid.

## 13. Physical Properties of Benzoic Acid

1. Benzoic acid is a white, crystalline compound (plate-like crystals), which melts at 122°C but sublimes when heated rapidly.

2. Its vapour has a peculiarly pungent odour which causes sneezing and coughing. In the solid state it has no odour.

3. It is only sparingly soluble in cold water, but it dissolves readily in hot water. It is also soluble in alcohol, ether, and benzene. When dissolved in benzene, it associates to form double molecules, $(C_6H_5.COOH)_2$.

4. It is volatile in steam.

## 14. Reactions of Benzoic Acid

Like all aromatic carboxylic acids, benzoic acid behaves very much like aliphatic carboxylic acids differing mainly in the reactions of the benzene ring part of the molecule. Thus, benzoic acid forms salts, esters, acid chlorides, and amides much in the same way as acetic acid. Owing to the influence of the electron-attracting benzene ring upon the carboxyl group attached to it, however, aromatic acids dissociate to a greater extent than the corresponding aliphatic carboxylic acids. This is why benzoic acid is a much stronger acid than acetic acid.

The chemical reactions of benzoic acid may be divided into two general classes : (1) those which are due to the —COOH group, and (2) those which produce substitution on the benzene ring (note that —COOH group is meta-directing).

**A. Reactions of the —COOH group.** These are :

1. *Formation of salts.* Benzoic acid is a weak monobasic acid which forms salts, called benzoates, with alkalis and carbonates.

$$\underset{\text{benzoic acid}}{C_6H_5.COOH} + NaOH \longrightarrow \underset{\text{sodium benzoate}}{C_6H_5.COONa} + H_2O$$

$$2C_6H_5.COOH + Na_2CO_3 \longrightarrow 2C_6H_5.COONa + H_2O + CO_2\uparrow$$

2. *Formation of esters.* When heated with an alcohol in the presence of a suitable dehydrating agent, benzoic acid forms the

corresponding esters, *e.g.*, ethyl benzoate with ethyl alcohol.

$$\underset{\text{benxoic acid}}{C_6H_5.COOH} + \underset{\text{ethyl alcohol}}{C_2H_5.OH} \xrightarrow{H_2SO_4} \underset{\text{ethyl benzoate}}{C_6H_5.COO.C_2H_5} + H_2O$$

3. *Formation of acid chloride*. When treated with phosphorus pentachloride benzoic acid yields benzoyl chloride.

$$\underset{\text{benzoic acid}}{C_6H_5.COOH} + PCl_5 \longrightarrow \underset{\text{benzoyl chloride}}{C_6H_5.COCl} + POCl_3 + HCl$$

4. *Formation of acid amide*. Benzoic reacts with ammonia to give ammonium benzoate, which, upon heating loses water yielding benzamide.

$$\underset{\text{benzoic acid}}{C_6H_5.COOH} + NH_3 \rightarrow \underset{\text{ammonium benzoate}}{C_6H_5.COONH_4} \xrightarrow{\Delta} \underset{\text{benzamide}}{C_6H_5.CONH_2} + H_2O$$

5. *Decarboxylation*. When sodium benzoate is heated with soda-lime, it is decarboxylated to give benzene.

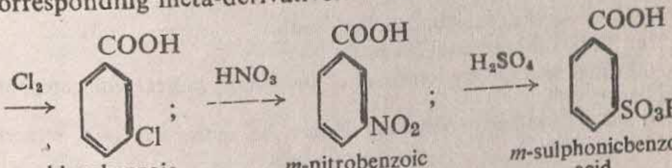
$$\underset{\text{sodium benzoate}}{C_6H_5.COONa} + NaOH \xrightarrow{\Delta} \underset{\text{benzene}}{C_6H_6} + Na_2CO_3$$

6. *Reduction*. When reduced with lithium aluminium hydride, benzoic acid gives benzyl alcohol

$$\underset{\text{benzoic acid}}{C_6H_5.COOH} + 4[H] \longrightarrow \underset{\text{benzyl alcohol}}{C_6H_5.CH_2OH} + H_2O$$

**B. Substitution reactions of the benzene ring**

7. *Halogenation, nitration, and sulphonation*. Benzoic acid undergoes these substitution reactions in the usual manner forming the corresponding meta-derivatives. Thus,



*m*-chlorobenzoic acid; *m*-nitrobenzoic acid; *m*-sulphonicbenzoic acid

## 15. Tests for Benzoic Acid

1. Benzoic acid dissolves in hot water, but separates out as pearly flakes upon cooling the solution.

2. It produces brisk effervesence with sodium carbonate solution owning to the evolution of carbon dioxide.

3. A neutralized solution of benzoic acid gives a buff precipitate of ferric benzoate with neutral ferric chloride solution.

4. When heated with ethyl alcohol and a little concentrated sulphuric acid, it forms ethyl benzoate which is recognized by its peppermint smell.

## 16. Uses of Benzoic Acid

1. *In medicine*, as primary antiseptic and in vapour form for disinfecting bronchial tubes.

2. For making benzoyl chloride, dyes, perfumes, and rust inhibitors.

3. As a preservative in processed foods (*e.g.*, tomato ketchup, jams, etc.) and fruit juices. However, sodium benzoate is preferred to benzoic acid for this purpose as it is less toxic.

### Questions

1. (*a*) What are phenols ? How are these different from aliphatic alcohols ?

(*b*) Describe any two methods for the preparation of phenol, and give balanced equations for the reactions.

(*c*) Name the product formed and write the equation for the reaction of phenol with bromine water.

(*d*) How would you convert phenol into picric acid.

(*e*) Write the structural formula of picric acid.

2. The following is a series of reactions. Study it carefully and answer the questions based on it :

$$\underset{A}{C_6H_6}+HCl+\tfrac{1}{2}O_2\xrightarrow[1]{}\underset{B}{C_6H_5Cl}+H_2O$$

$$\underset{B}{C_6H_5Cl}+Mg\xrightarrow[2]{\text{ether}}\underset{C}{C_6H_5MgCl}$$

$$\underset{C}{C_6H_5MgCl}+\tfrac{1}{2}O_2\xrightarrow[3]{}\underset{D}{C_6H_5OMgCl}$$

$$\underset{D}{C_6H_5OMgCl}+H_2O\xrightarrow[4]{}\underset{E}{C_6H_5OH}+Mg(OH)Cl$$

(*a*) Identify the compound A, B, C and E.

(*b*) Name the reactions (2) and (4)

(*c*) What will be the reaction of the $NO_2^+$ radical with compound A ? Name this reaction.

(*d*) Describe how compound E can be converted into phenylamine (aniline), $C_6H_5.NH_2$ ?

3. (*a*) How will you distinguish between phenol and ethyl alcohol ?

(*b*) How will you convert phenol into salicyclic acid ? Name the reaction.

4. (*a*) Give a method for the laboratory preparation of benzaldehyde.

(*b*) What are the products when benzaldehyde is

*i.* oxidized with acidified $KMnO_4$.
*ii.* reduced with sodium amalgam and water.
*iii.* warmed with KOH solution.

Give balanced equations for the reactions.

(*c*) Give a simple test to distinguish benzaldehyde from acetaldehyde.

5. (*a*) What happens when benzaldehyde reacts with—

*i.* concentrated sodium hydroxide solution ?
*ii.* acetic anhydride, sodium acetate, and heat ?
*iii.* alcoholic potassium cyanide ?

(*b*) Name the reactions (*e.g.*, Rosenmund reaction, aldol condensation, Perkin's reaction, Kolbe's reaction, Cannizaro reaction, etc.) in (*a*) and give the balanced equation for each reaction.

6. (*a*) How is benzoic acid made from toluene ? From benzaldehyde ? Give balanced equations for the reactions.

(*b*) Give the reactions of benzoic acid which depend on the presence of the —COOH group.

(*c*) Why is benzoic acid a stronger acid than acetic acid ?

7. What happens when—

*i.* $CO_2$ is passed into sodium phenate under pressure,
*ii.* sodium phenate reacts with methyl iodide,
*iii.* benzaldehyde is treated with fuming nitric acid,
*iv.* benzoic acid is reduced with lithium aluminium hydride ?

8. Show by means of equations only how you will convert—

*i.* benzene into phenol and phenol into benzene,
*ii.* benzene into benzoic acid and benzoic acid into benzene,
*iii.* phenol into picric acid,
*iv.* benzoic acid into benzoyl chloride ?

## Key

2. (*a*) A=benzene, B=chlorobenzene, C=phenylmagnesium chloride, E=phenol.

(*b*) Grinard reaction, hydrolysis.

(*c*) Nitrobenzene will form by nuclear substitution. The reaction is named nitration.

(*d*) By reaction with $NH_3$ in the presence of $ZnCl_2$ at 300°C.

3. (*a*) By treatment with a drop of aq. $FeCl_3$; phenol will develop violet coloration, no change in ethyl alcohol.

(*b*) By converting phenol into sodium phenate and heating the latter to about 200°C in carbon dioxide. The resulting sodium salicylate is hydrolysed to give salicylic acid.

$$\begin{tikzcd}
\underset{\text{phenol}}{C_6H_5OH} \arrow[r, "NaOH"] & \underset{\text{sodium phenate}}{C_6H_5.ONa} \arrow[r, "{CO_2,\ 200^\circ C}"] & \underset{\text{sodium salicylate}}{C_6H_4.(ONa).COOH} \arrow[d, "HOH"] \\
 & & \underset{\text{salicylic acid}}{C_6H_4(OH).COOH}
\end{tikzcd}$$

The reaction is called Kolbe's reaction.

5. (*b*) Reaction (*i*) Cannizaro reaction; Reaction (*ii*) Perkin's reaction; and Reaction (*iii*) aldol condensation.

□ □

# 31

# Polymers

The various stages of human civilization are broadly referred to by the materials used by man during different ages to help him in his struggle to survive. Thus, there have been the *stone age*, the *copper age*, the *bronze age*, and the *iron age* The general pattern has been that the more versatile the material man has had at his disposal, the more advanced his civilization has become. Today man has at his disposal a highly versatile range of materials, called *synthetic polymers*, from which are fabricated a wide variety of products ranging from tiny buttons to huge motor boats. When polymers are fabricated into useful articles they are referred to as *plastics*, *rubbers*, and *fibres*. We are living in the Age of Synthetic Polymers. A list of names of the better known materials of this class would include Bakelite, polythene, polystyrene, teflon, nylone, terylene, PVC, etc. All of these are purely synthetic polymers in contrast to the natural polymers such as cotton and wool or the semi-synthetic polymers such as rayon and Celanese derived from the natural polymers.

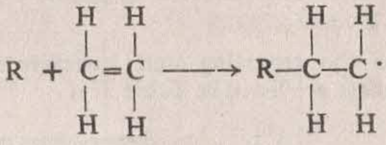
## 1. Some Definitions

**A polymer** is a substance of high molecular weight formed by the chemical union of many low-molecular-weight molecules of one single substance or of two or more different substances. There is no agreement as to the minimum molecular weight a substance must have in order for it to be called a polymer. However, a practical figure would be about 2500. The molecular weights of common polymers vary from about 20,000 (*e g*., nylon) to several hundred thousand (*e.g.*, polyvinyl chloride, 250,000). The process of building up a polymer from simple molecules is termed *polymerization*. Polymerization is best defined as *intermolecular combinations that can theoretically proceed without limit*. In practice, however, the polymer ceases to grow after a certain stage. A compound capable of conversion into a polymer, as ethylene into polyethylene, is called a *monomer* (*mono*, one; *mer*, unit) A polymer then is a molecule, of many units and is also known as a **macromolecule**.

## 2. Types of Polymerization

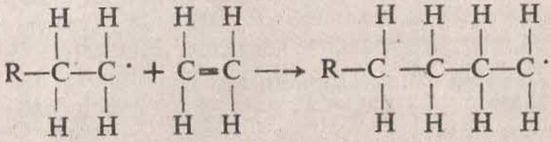
There are two main types of polymerization : *addition polymerization and condensation polymerization*.

**2-1. Addition polymerization.** Addition polymerization involves self-combination of a large number of monomer units without the elimination of small molecules. The empirical formula of the resulting polymer is the same as that of the monomer. The monomer is generally an unsaturated organic compound such as ethylene, $CH_2{=}CH_2$. The mechanism of polymerization involves the rupture of the carbon-carbon double bond by the action of a free redical generated by the catalyst, such as benzoyl peroxide. This compound, at high temperatures and pressures, splits and each half of the molecule comes apart carrying a spare electron*. This may be represented as $R : R \rightarrow R^{\cdot} + {}^{\cdot}R$, where $R^{\cdot}$ is a free radical. This free radical attacks an ethylene molecule thus :



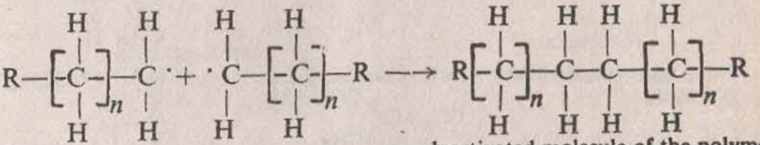
$$R + \underset{H}{\overset{H}{C}}{=}\underset{H}{\overset{H}{C}} \longrightarrow R{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{}^{\cdot}$$

An electron from the double bond (it is made up of a pair of shared electrons) is pulled over to join the electron on C to form a bond. This leaves the other electron of the double bond spare. The free radical has thus generated another free radical of the ethylene molecule, which can then generate another.



$$R{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{}^{\cdot} + \underset{H}{\overset{H}{C}}{=}\underset{H}{\overset{H}{C}} \longrightarrow R{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{}^{\cdot}$$

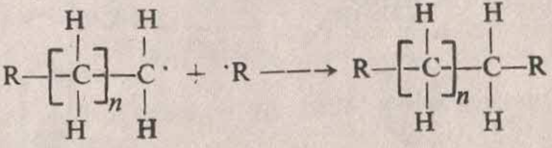
A large number of molecules are involved in succession forming a long chain. The process may come to stop in several ways. Two possible ways are : (1) by the collision between two growing chains which unite to form a deactivated molecule,



$$R{-}\left[{-}\underset{H}{\overset{H}{C}}{-}\right]_n{-}\underset{H}{\overset{H}{C}}{}^{\cdot} + {}^{\cdot}\underset{H}{\overset{H}{C}}{-}\left[{-}\underset{H}{\overset{H}{C}}{-}\right]_n{-}R \longrightarrow R\left[{-}\underset{H}{\overset{H}{C}}{-}\right]_n{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\left[{-}\underset{H}{\overset{H}{C}}{-}\right]_n{-}R$$

deactivated molecule of the polymer

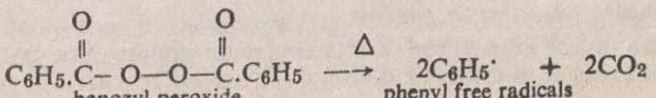
and (2) by the collision of the growing chain and a catalyst radical $R^{\cdot}$.



$$R{-}\left[{-}\underset{H}{\overset{H}{C}}{-}\right]_n{-}\underset{H}{\overset{H}{C}}{}^{\cdot} + {}^{\cdot}R \longrightarrow R{-}\left[{-}\underset{H}{\overset{H}{C}}{-}\right]_n{-}\underset{H}{\overset{H}{C}}{-}R$$

---

[*]



$$C_6H_5.\overset{O}{\overset{\|}{C}}{-}O{-}O{-}\overset{O}{\overset{\|}{C}}.C_6H_5 \xrightarrow{\Delta} 2C_6H_5^{\cdot} + 2CO_2$$

benozyl peroxide phenyl free radicals

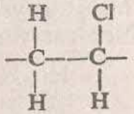
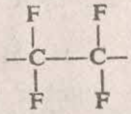
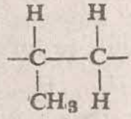
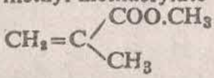
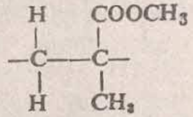
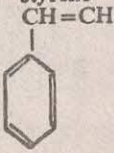
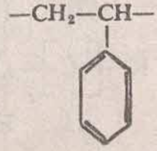
The polymerization of ethylene to polyethylene is more simply represented as :

$$n\underset{\text{ethylene}}{CH_2=CH_2} \xrightarrow{\text{catalyst}} \underset{\text{polyethylene}}{(-CH_2-CH_2-)_n}$$

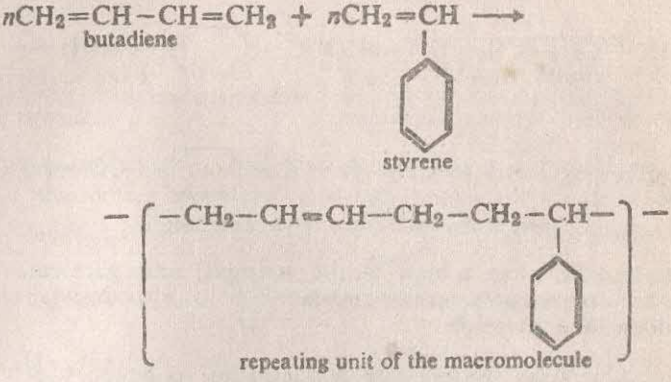
In general, the polymers may be represented by the general structural formula $X[A]_nY$, in which A is called the 'repeating unit' and X and Y the 'end groups'. The repeating unit A is a group of atoms (carbon being essentially one of these) which may be simple like $-CH_2-$ as in ethylene, or much more complex. Although the term polymer is used synonymously with macromolecule, it may be appreciated that the former term denotes a succession of identical repeating units without the end groups.

The monomer and the repeating unit structure of some more common addition polymers are listed in Table 31-1.

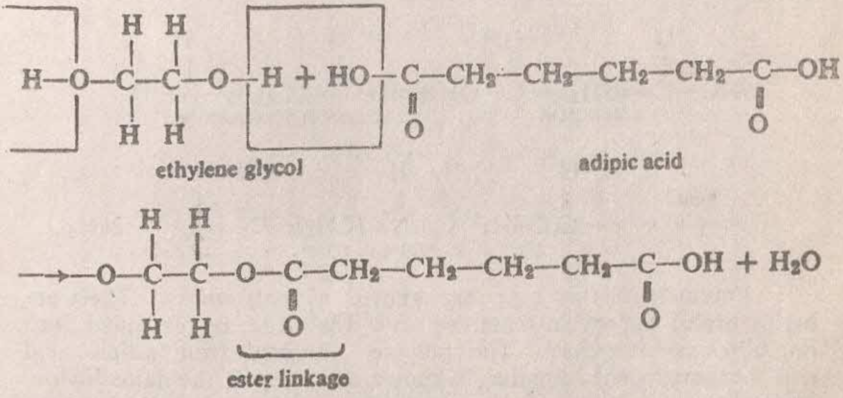
**Table 31-1** *Some common addition polymers*

| Name of the polymer | Monomer | Repeating unit structure |
|---|---|---|
| 1. Polyvinylchloride (P.V.C.) | Vinyl chloride, $CH_2=CHCl$ |  $-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-$ |
| 2. Polyterafluoroethylene (P.T.F.E.), Teflon | tetrafluoroethylene $CF_2=CF_2$ |  $-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-$ |
| 3. Polypropylene | propylene $CH_3.CH=CH_2$ |  $-\overset{H}{\underset{CH_3}{C}}-\overset{H}{\underset{H}{C}}-$ |
| 4. Polymethyl methacrylate (Perspex) | methyl methacrylate  $CH_2=C{\genfrac{}{}{0pt}{}{COO.CH_3}{CH_3}}$ |  $-\overset{H}{\underset{H}{C}}-\overset{COOCH_3}{\underset{CH_3}{C}}-$ |
| 5. Polystyrene | styrene  |  |

*Copolymerization.* Addition polymerization is not limited to molecules of one kind, it can also take place among two or more different kinds of monomer molecules. In the latter case, the phenomenon is known as *copolymerization* or *interpolymerization*. Many synthetic rubbers are polymers of butadiene, $CH_2=CH-CH=CH_2$, copolymerized with other addition-type monomers, *e.g.*, styrene.


$nCH_2=CH-CH=CH_2 + nCH_2=CH \longrightarrow$
butadiene
styrene
$-[-CH_2-CH=CH-CH_2-CH_2-CH-]-$
repeating unit of the macromolecule

**2-2. Condensation polymerization.** Condensation polymerization takes place between two monomer units, each containing two or more functional groups. The bi- or polyfunctional molecules condense with one another repeatedly, eliminating a small molecule such as water, ammonia, etc., as the reaction proceeds. For example ethylene glycol, $HO.CH_2.CH_2.OH$, and adipic acid, $COOH.CH_2.CH_2.CH_2.CH_2.COOH$, undergo condensation polymerization as the result of the formation of ester linkages. The equation below shows the first stage of this process.

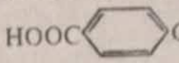


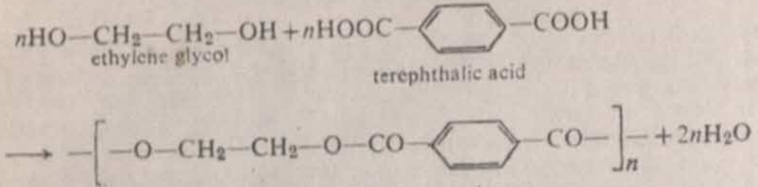
$$\underbrace{H-O-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O-H}_{\text{ethylene glycol}} + \underbrace{HO-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-OH}_{\text{adipic acid}}$$

$$\longrightarrow -O-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\underbrace{O-\underset{\underset{O}{\|}}{C}}_{\text{ester linkage}}-CH_2-CH_2-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-OH + H_2O$$

The polymers of this type are called *polyesters*, and are widely used as synthetic fibres.

Three well known polymers, produced by condensation polymerization are *terylene* (also called decron or terene), nylon, and Bakelite.

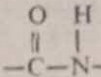
(1) *Terylene.* The monomers for terylene, a polyester, are ethylene glycol, $HO.CH_2.CH_2.OH$, a dihydroxy alcohol, and terephthalic acid, , a dicarboxylic acid.

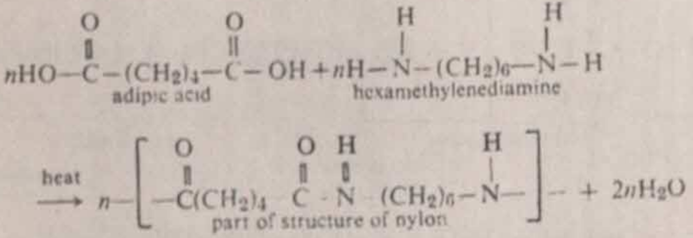


part of the structure of terylene or dacron

Terylene fibre has a high tensile strength, and garments made of it are remarkably crease-resistant. It is also resistant to moths, mildew, and abrasion.

(2) *Nylon.* Nylon, the condensation polymer widely used in plastics and fabrics is made from adipic acid, $HOOC-CH_2-CH_2-CH_2-CH_2-COOH$, and hexamethylenediamine, $NH_2-CH_2\cdot CH_2-CH_2-CH_2-CH_2-CH_2-NH_2$. The reaction by which these monomer units become bonded together is a conventional amide formation accompained by elimination of water. However, owing to the presence of reacting groups ($-COOH$ and $-NH_2$) these molecules can react repeatedly, each time removing water, and forming amide

linkages,  $-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-$ at both ends.



$$n\mathrm{HO}-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-OH+n\mathrm{H}-\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}-H$$

$$\xrightarrow{\text{heat}} n-\left[-\overset{\overset{O}{\|}}{C}(CH_2)_4\ \overset{\overset{O}{\|}}{C}\cdot\overset{\overset{H}{|}}{N}\ (CH_2)_6-\overset{\overset{H}{|}}{N}-\right]-+2nH_2O$$

part of structure of nylon

Polymers of this type are known as *polyamides.* These are highly useful as textile materials since they can be extruded into fine fibres and stretched. The polymer obtained from adipic acid and hexamethylene diamine is known as nylon-66, the name 'nylon' being the class name of the polyamides. Other polyamides can be made from other dicarboxylic acids and other diamines. Thus 'nylons' of widely varying properties suited to a variety of uses can be produced.

Nylon is fabricated into sheets, bristles, and textile fibres. The long chain molecules have a random arrangement in an undrawn nylon fibre (Fig. 31-1*a*), but when streched, the molecules line up into approximately parallel positions to give a very tough fibre. (Fig. 31-1*b*).

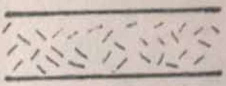


Fig. 31-1 (*a*) Undrawn nylon fibre (random arrangement of molecules)

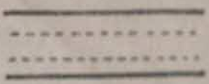
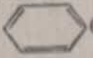
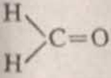
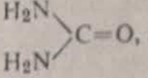
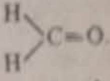
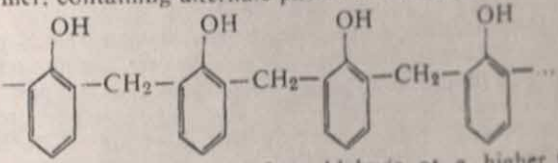


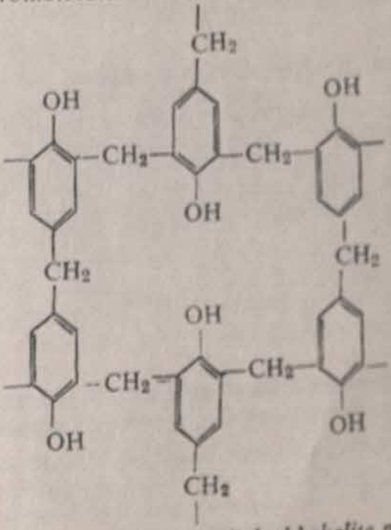
Fig. 31-1 (*b*) Nylon fibre streched several times to its original length (molecules oriented in parallel positions).

3. *Bakelite.* The Bakelite type of polymers are made from two kinds of monomers which can contribute to the formation of water. Two combinations are : (*a*) phenol,  OH, and formaldehyde,  $H_2C{=}O$, and (*b*) urea,  $(H_2N)_2C{=}O$, and formaldehyde,  $H_2C{=}O$.

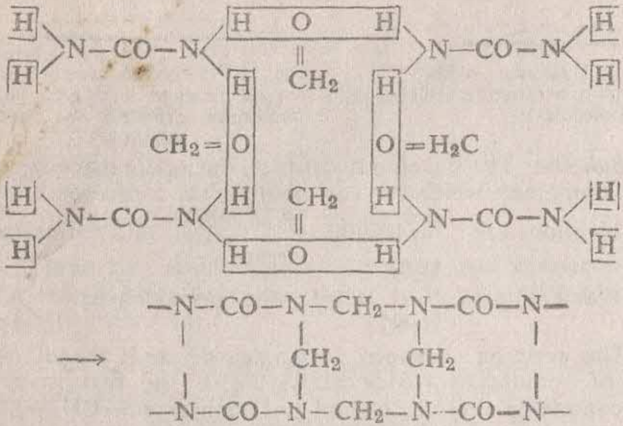
*a.* The reaction between formaldehyde and phenol (in the presence of sodium hydroxide catalyst) give rise first to a *linear* polymer, containing alternate phenol and methylene ($-CH_2-$) units :



Subsequently, with more formaldehyde at a higher temperatures, linear structures interwine by cross-linkages to gives three-dimensional cage of macromolecules :



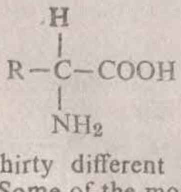
*part of the structure of the cross-linked bakelite polymer* *b*. The Bakelite type polymers from urea, $NH_2.CO.NH_2$, and formaldehyde, $CH_2{=}O$ are known as *urea-formaldehyde resins*. The following represents a small section of a cross-linked polymer of this type :



It should now be clearly appreciated that the principle of polymerization is based on the multifunctional nature of the monomers. A monofunctional substance such, as ethyl alcohol, is incapable of polymerization because it contains only one functional group that is used up in a chemical reaction with another molecule. Condensation polymerization occurs between such bifunctional reacting monomers as ethylene glycol and terephthalic acid, hexamethylenediamine and adipic acid, etc. In addition polymerization, the double bond in the monomer acts as a bifunctional unit causing repeated union.

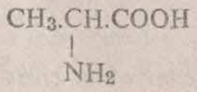
## 3. Proteins, Natural Polyamides

Proteins, the essential constituents of all living cells are structurally the polyamides. The monomeric units are the α-amino acids, which contain an amino group, $-NH_2$, attached to the α-carbon, *i.e.*, the carbon atom immediately adjacent to the carboxyl group. These can be represented by the general formula

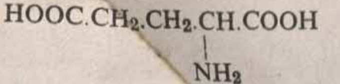


$$R-\overset{\substack{H\\|}}{\underset{\substack{|\\NH_2}}{C}}-COOH$$

There are nearly thirty different amino acids involved in the formation of proteins. Some of the more common of these are :

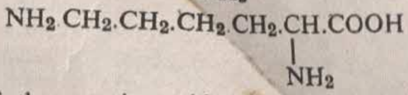
| | |
|---|---|
| 1. Glycine | $NH_2.CH_2.COOH$ |
| 2. Alanine |  $CH_3.\underset{\substack{|\\NH_2}}{CH}.COOH$ |

3. Glutamic acid



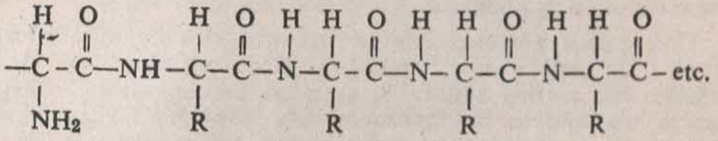
$$HOOC.CH_2.CH_2.\underset{\underset{NH_2}{|}}{CH}.COOH$$

4. Lvcine



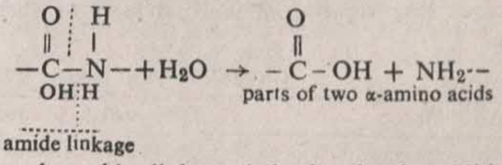
$$NH_2.CH_2.CH_2.CH_2.CH_2.\underset{\underset{NH_2}{|}}{CH}.COOH$$

The polymerization of the $\alpha$-amino acids to proteins involves the condensation of the $-NH_2$ group of one acid with the carboxyl group of another, setting up an amide linkage, $-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-$, by the loss of a water molecule from the two amino acids. In the case of the amino acid monomers this linkage is called a *peptide linkage* or a *peptide bond.* The protein molecule may involve hundreds of amino acid molecules bonded through the amide or peptide linkages. A portion of this chain may be represented as shown below :



$$-\underset{\underset{NH_2}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-NH-\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-\text{etc.}$$

When a protein is hydrolysed the amide linkage is broken, yielding the constituent amino acids.



$$-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-+H_2O \rightarrow -\overset{\overset{O}{\|}}{C}-OH + NH_2\text{-}-$$

Since each amide linkage is broken by the addition of a molecule of water, the total weight of amino acids obtained is greater than the weight of the protein hydrolyzed.

A large number of proteins are known; different living species of plants and animals have in their tissues a great many different proteins. Enzymes, the biological catalysts, are also proteins and so are the natural fibres, wool and silk. The molecular weight of individual proteins varies tremendously, for a low of about 10,000 to a high of several millions. Since the thirty natural amino acids can combine in long chains of a hundred or more molecules in countless different ways, it is not surprising that proteins occur in such a wide variety.

## 4. Effect of Chain Length and Cross-Linking on Physical Properties of Polymers

Depending on their molecular structures, the polymers are of two types : linear polymers and cross-linked polymers. In linear polymers, such as polyethylene, the monomeric units are arranged in a single dimension; in cross-linked polymers, such as Bakelite, the arrangement is three-dimensional. The linear polymers are soluble in many organic solvents (hence, some of these are used to make paints and lacquers); cross-linked polymers are insoluble in any kind of solvents. In general, the effects of increasing the chain-length are increased resistance to the solvent action of common solvents and also to the chemical action of acids and alkalis. Cross-linked polymers are chemically inert.

Linear and cross-linked polymers most significantly differ in their behaviour on heating. Linear polymers soften whenever heated and harden again on cooling to room temperature. These are said to be **thermoplastic**. When heated, thermoplastics can be easily moulded, extruded into fibres, or rolled into sheets. The process of heat-softening, moulding. and cooling can be repeated as often as desired, and hardly affects the properties of these polymers. From your own experience you will have noted these properties in many everyday-use articles. Hot tea in a plastic cup makes it less rigid PVC pipes become soft when left in bright sun. What happens if hot iron is put on nylon fabrics ?

Cross-linked polymers can be heat-treated only once before they set, *i.e.*, before their formation. Once set, they lose their plasticity, and heating results in chemical decomposition. These polymers are said to be **thermosetting plastics**. Their rigid structure is the result of the polymerization taking place in three dimensions to give a firm cage of molecules.

Table 31-2 lists some common polymers as thermoplastic or thermosetting.

**Table 31-2** *Classification of some common polymers*

| *Thermoplastic (linear)* | *Thermosetting (cross-linked polymers)* |
|---|---|
| 1. Polyethylene, polythene | 1. Phenol-formaldehyde (Bakelite) |
| 2. Polyvinylchloride. P.V.C. | 2. Urea—formaldehyde |
| 3. Polystyrene | 3. Resorcinol*—formaldehyde |
| 4. Polytetrafluorethylene (P.T.F E), teflon | 4. Melamine†—formaldehyde (Formica) |
| 5 Polymethylmethacrylate, 'perspex' | |
| 6 Polyethylene terephthalate (terylene) | |
| 7. Poly-hexamethylene adipamide (nylon). | |

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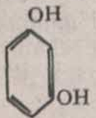
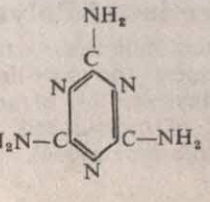
*Resorcinol is a dihydric phenol,



†Melamine is a cyclic compound containing three amino groups :



## 5. Synthetic Fibres

**Fibres** may be defined as solid materials whose lengths are hundreds or thousands of times greater than their widths and which, in spite of this characteristic, are sufficiently strong, pliable, and resistant to abrasion. They are used to make textiles, ropes and twines, and industrial and furnishing fabrics. In a narrower sense, the textile fibres may be described as filamentry solids whose molecules are oriented lengthwise, *i.e.*, along their major dimension.

The natural textile fibres are of two kinds : (1) *cellulose fibres e.g.*, cotton, linen, flax, hemp, and jute, derived from plant sources, and (2) *protein fibres*, *e.g.*, silk and wool, derived from animal sources. The textile fibres called rayons can be called *artificial fibres* or *semi-synthetic fibres*. These are not synthetic fibres in the true sense as their high molecular weight structure is present in the starting natural material, cellulose or cotton. *Synthetic fibres* came into existence with the development of polymerization processes.

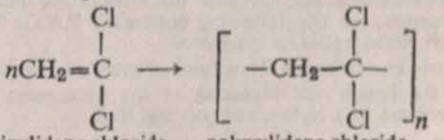
The first truly synthetic fibre to become commercially important was *nylon*. As described earlier, it is a condensation polymer made from a six carbon diamine (hexamethylene diamine) and a six-carbon dicarboxylic acid, adipic acid. Nylon has some of the properties of silk. It is widely used as a fibre and also for tyre cords.

Other synthetic fibres are terylene, orlon, vinyon, velon, etc. Terylene (or dacron) is a polyester made from ethylene glycol and terephthalic acid, and has been already described. The fibre has a high tensite strength, and garments made of it are remarkably crease-resistant. Alone, or blended with long fibre Egyptian cotton, it makes a quick-drying fabric for shirts, blouses, and suits that requires little ironing

*Orlon* is a highly polymerized acrylonitrile, $CH_2{=}CHCN$. Textiles made from it resemble either wool or silk and feel warm to the hand. Orlon yarn is knitted into fine sweaters.

*Vinyon* is made by the condensation polymerization of vinyl chloride, $CH_2{=}CHCl$, and vinyl acetate, $CH_2{=}CH.OOC.CH_3$. It withstands acids, water, and chemicals particularly well.

*Velon* is a highly polymerized vinylidene chloride, $CH_2{=}CCl_2$. The polymerization proceeds similarly to that of vinyl chloride :



$$n\mathrm{CH_2{=}}\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{C}}} \longrightarrow \left[-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{C}}}-\right]_n$$

vinylidene chloride polyvylidene chloride (*velon*)

Velon is not affected by sun and perspiration.

**5-1. Superiority of synthetic fibres.** The synthetic textile fibres are superior to the natural or semisynthetic fibres in several respects. They are tough, wear well, shrink little, can be washed easily, and are not affected by mildew and clothes moths. They are not injured by water or dry cleaning solvents. Most of them possess excellent dyeability. In many cases they resist the chemical action of acids, alkalis, etc. And above all, synthetic fibres can be created with custom-built properties to meet the needs of a wide variety of uses.

**5-2. Identifying fibres**. Many natural and synthetic fibres can be easily identified by the so called 'burning test'. Hold a piece of the fabric in a non-luminous Bunsen flame. Watch carefully what happens, and identify the fibre with the help of Table 31-3.

**Table 31-3** *Identifying common fibres*

| *Fibre* | *Observations in the burning test* |
|---|---|
| 1. Cotton | Burn vigorously, smell of burning paper, no bead formed. |
| 2. Viscose rayon | |
| 3. Wool | Burn with difficulty, smell of burning paper, no bead formed. |
| 4. Silk | |
| 5. Acetate rayon | Burns, fabric shrinks from flame, smell of vinegar, black bead formed which is easily crushed. |
| 6. Nylon | Burns with difficulty, fabric shrinks from flame, smell of burning hair, hard round bead formed which cannot be crushed. |
| 7. Terylene | Like nylon, but burns with black, sooty smoke. |
| 8. Orlon | Burns with a sooty flame, fabric shrinks from flame, black bead forms which is easily crushed. |

## Questions

1. (*a*) Define the terms *polymer*, *polymerization*, and *macromolecule*.

(*b*) What do you understand by (*i*) addition polymerization, and

(*ii*) condensation polymerization ?

2. Two methods of making artificial fibres and plastics are *addition polymerization* and *condensation polymerization*.

(*a*) What chemical feature must the monomer show for addition polymerization to take place ?

(*b*) Give one example of a polymer made by this process.

(*c*) What is the essential chemical feature of condensation polymerization.

(*d*) Give one example of a polymer made by this process.

3. (*a*) Give the names and chemical formulae of the monomers and of the repeating unit structures of the following polymers: P.V.C., P.T.F.E., polypropylene, polymethyl methacrylate, polystyrene.

(*b*) Give one example each for natural polymer and synthetic polymer.

(*c*) Give the names and formulae of the monomers for the following polymers: (*i*) Terylene, (*ii*) Nylon, and (*iii*) Bakelite.

4. (*a*) Describe by means of chemical formulae the formation of peptide linkage.

(*b*) What are the products of the hydrolysis of proteins ? Why do the products weigh more than the protein hydrolyzed ?

5. (*a*) What are thermosetting and thermoplastic polymers ? Give four examples of each.

(*b*) Write a short note on 'synthetic fibres'.

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